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EDITED BY
Nicola Maria Pugno,
University of Trento, Italy

REVIEWED BY
Abdulkareem Omeiza Yusuf,
Missouri University of Science and Technology, United States

*CORRESPONDENCE
Yong-Sik Chu,
yschu@kicet.re.kr
Jang-Ho Jay Kim,
jjhkim@yonsei.ac.kr

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Calcium fluoride as an efficient mineralizer for low-temperature portland cement clinkering: a mechanistic mini review

Bilguun Mend[1,2], Youngjun Lee[1], Do-Young Kwon[1], Jang-Ho Jay Kim[2]* and Yong-Sik Chu[1]*

[1]Climate and Energy R&D Group, Korea Institute of Ceramic Engineering and Technology, Jinju, Republic of Korea, [2]School of Civil and Environmental Engineering, Yonsei University, Seoul, Republic of Korea

Reducing the clinkering temperature of Portland cement is a key strategy for lowering energy consumption and CO_2 emissions. Among various mineralizers, calcium fluoride (CaF_2) has been widely reported as an effective additive for promoting clinker formation at reduced temperatures. This mini review summarizes recent mechanistic insights into the role of CaF_2 in facilitating low temperature alite (C_3S) formation. Available evidence suggests that CaF_2 exerts its mineralizing effect through interconnected mechanisms, including enhanced lattice defect formation, accelerated ionic diffusion, and early liquid-phase development. Fluoride ions (F^-) are proposed to substitute for oxygen sites in the C_3S structure, generating calcium vacancies that facilitate the C_2S-to-C_3S transformation at lower temperatures. At the melt scale, CaF_2 reduces melting temperature and viscosity, thereby improving ionic transport and phase combination. CaF_2 addition is also frequently associated with the preferential formation of high symmetry alite polymorphs under reduced thermal conditions. When combined with metal oxides such as TiO_2, CuO, and ZnO, CaF_2 often exhibits synergistic effects that further enhance clinker formation efficiency. In addition, waste-derived CaF_2 has been shown to retain mineralizing activity comparable to natural fluorite, supporting resource efficiency and circular-economy approaches. Overall, CaF_2 is a promising mineralizer for low-temperature, energy-efficient, and low-carbon cement manufacturing, while its effectiveness remains system-dependent.

KEYWORDS

alite formation, calcium fluoride, low-temperature clinkering, mineralizers, sustainable cement, alite polymorphs, clinker mineralization

1 Introduction

Portland cement production is among the most energy-intensive industrial processes worldwide and is responsible for approximately 7%–8% of global anthropogenic CO_2 emissions (Zhang et al., 2021; Khalil and AbouZeid, 2025; Zong et al., 2025). This substantial environmental burden is primarily associated with the high temperatures required for clinker formation (Abdul et al., 2025), typically in the range of 1450 °C–1500 °C, to ensure sufficient development of tricalcium silicate (C_3S, alite) (Ouzia and Scrivener, 2019), the principal phase governing early-age strength of cement (Martin et al., 2024). In response to increasing regulatory pressure and global decarbonization targets, reducing the clinkering temperature has emerged as a key strategy for lowering thermal energy demand, fuel consumption, and process-related CO_2 emissions in the cement industry (Han et al., 2026; Zapata and Bosch, 2009; Hafiz et al., 2020; Qian et al., 2016; Li et al., 2022; Wang et al., 2024; Igami et al., 2025). Within this framework, the use of mineralizers has attracted significant attention as an effective and industrially feasible approach to enhance clinker burnability (Song et al., 2026). Mineralizers facilitate clinker formation by increasing raw-meal reactivity, promoting early liquid-phase formation, and accelerating phase transformations under reduced thermal input (Lin et al., 2025; Amare et al., 2025). Among the various mineralizing agents investigated, calcium fluoride (CaF_2) has been widely reported as an effective mineralizer for lowering clinkering temperature while maintaining or improving clinker quality (Dahhou et al., 2021) It should be noted that reported reductions in clinkering temperature are highly system-dependent and vary with raw-meal composition, co-dopants, and the criteria used to define clinker formation. In this context, previous studies have shown that CaF_2-containing systems can exhibit apparent temperature reductions on the order of ~100 °C in ordinary Portland cement and up to ~100 °C–300 °C in belite-rich compositions, reflecting combined compositional and process-related effects rather than the isolated action of CaF_2 alone.

The pronounced mineralizing effect of CaF_2 arises from several interconnected mechanisms operating at both lattice and melt scales. At the lattice level, fluoride ions (F^-) substitute for non-bridging oxygen sites within the C_3S crystal structure, leading to the formation of calcium vacancies and an increased concentration of lattice defects (Da et al., 2022a). These defects enhance ionic mobility and lower the activation energy for cation diffusion, thereby facilitating the solid-state transformation of dicalcium silicate (C_2S) into C_3S at reduced temperatures (Guan et al., 2025; Yang et al., 2024; Li et al., 2024). At the melt level, CaF_2 lowers the liquidus temperature and reduces melt viscosity, enabling earlier formation of a fluid phase that enhances mass transport and accelerates the incorporation of CaO into silicate phases (Tao et al., 2025; Hu et al., 2025; Guo et al., 2025). In addition, CaF_2 promotes the formation and stabilization of high-symmetry alite polymorphs, such as monoclinic and rhombohedral C_3S, which preferentially crystallize under lower thermal conditions and exhibit superior burnability compared to low-symmetry counterparts.

In recent years, the relevance of CaF_2 mineralization has been further strengthened by advances in waste valorization. Industrial sludges generated from semiconductor processing, photovoltaic manufacturing, and metal pickling frequently contain high proportions of CaF_2, typically ranging from 40 to 60 wt% (Banshchikov et al., 2023; Wu et al., 2024; Zhang et al., 2025; Thakur et al., 2026; Shtan'ko et al., 2020). Experimental and industrial studies have demonstrated that waste-derived CaF_2 retains mineralizing performance comparable to that of natural fluorite, while simultaneously enabling the immobilization of fluorine and heavy metals within clinker mineral phases.

This dual functionality supports circular-economy strategies by reducing reliance on virgin raw materials and providing a safe pathway for the co-processing of fluoride-bearing industrial wastes. Despite these advantages, the application of CaF_2 requires careful optimization. Excessive fluorine content may result in the formation of insoluble CaF_2-rich surface layers on clinker minerals, potentially inhibiting early hydration. Most studies report an optimal CaF_2 dosage in the range of 1–3 wt%, depending on raw-meal composition and coexisting oxides (Wang et al., 2021; Kulikov et al., 2024). Moreover, the presence of metal oxides such as TiO_2, ZnO, and CuO can either enhance or suppress the mineralizing effect of CaF_2 through synergistic or competitive interactions, underscoring the need for a mechanistic understanding of multi-component systems.

Accordingly, this mini review critically synthesizes recent advances in understanding the role of CaF_2 in reducing the clinkering temperature of Portland cement. Special attention is given to distinguishing between kinetic accessibility and thermodynamic considerations in reported CaF_2-assisted mineralization mechanisms. Emphasis is placed on lattice-level defect chemistry, melt-phase behavior, alite polymorph stabilization, and synergistic effects arising from co-doping with metal oxides and waste-derived additives. The objective is to provide both a mechanistic framework and practical insights to support the industrial implementation of CaF_2-based mineralization strategies for low-temperature, energy-efficient, and low-carbon cement production.

2 Mechanism of CaF_2 mineralization

2.1 Lattice-level effects

Fluoride ion substitution within the crystal structure of tricalcium silicate (C_3S) has been widely proposed as an important lattice-level contribution to CaF_2-assisted mineralization. Boughanmi et al. (2018) reported that fluoride ions (F^-) can preferentially replace non-bridging oxygen sites in the C_3S lattice, leading to the formation of charge-compensating calcium vacancies and an increase in lattice disorder. Such defect formation is commonly inferred from indirect experimental observations, including X-ray diffraction peak shifts and Fourier-transform infrared band broadening in CaF_2-containing systems.

The resulting increase in defect concentration is generally interpreted as facilitating ionic mobility within the silicate framework, thereby lowering the kinetic barriers associated with cation diffusion and solid-state phase transformation. In this context, Da et al. (2021a) showed that CaF_2-doped systems exhibit accelerated conversion of dicalcium silicate (C_2S) to C_3S at temperatures approximately 50 °C–100 °C lower than those required under conventional clinkering conditions. While the available evidence does not establish a single dominant mechanism, these observations are consistent with the view that fluoride-induced lattice defects contribute to enhanced alite nucleation and growth, particularly when coupled with concurrent melt-phase effects.

2.2 Melt-phase behavior

Modification of melt-phase characteristics is widely regarded as an important contribution to the mineralizing effect of CaF_2 in Portland cement systems. Previous studies have reported that the addition of CaF_2 can lower the liquidus temperature and reduce melt viscosity, thereby promoting earlier formation of a fluid phase during clinkering (Guo et al., 2025; Banshchikov et al., 2023). Under such conditions, mass transport is facilitated through viscous flow within the melt rather than being limited by solid-state diffusion, which can accelerate clinker phase formation at reduced temperatures.

Experimental observations by Da et al. (2021b) indicated that CaF_2-containing raw meals exhibit earlier liquid-phase formation compared with CaF_2-free systems, which is consistent with enhanced ionic transport and more efficient incorporation of CaO into silicate phases. In addition, reduced melt viscosity has been associated with improved solid–liquid interfacial contact, facilitating dissolution–precipitation processes and contributing to lower free-lime contents (Laonamsai et al., 2025).

This melt-assisted behavior appears to be particularly relevant in belite-rich and low-basicity systems. For example, Dahhou et al. (2021) reported substantial reductions in optimal firing temperature in belite-rich clinkers containing CaF_2, which they attributed to early melt formation and enhanced phase combination kinetics. Similarly, recent studies on waste-derived CaF_2 sources suggest that melt-modifying effects comparable to those of natural fluorite can be achieved despite compositional complexity (Mend et al., 2025).

Overall, available evidence suggests that melt-phase modification by CaF_2 contributes to improved diffusion kinetics and phase development under reduced thermal input, while its effectiveness remains strongly dependent on system composition, coexisting oxides, and processing conditions.

2.3 Polymorph stabilization

The formation of high-symmetry alite polymorphs in CaF_2-containing systems has been widely reported in the literature and is commonly associated with improved clinker burnability under reduced thermal conditions. In conventional CaF_2-free systems, alite typically crystallizes as low-symmetry triclinic polymorphs at lower temperatures, whereas monoclinic and rhombohedral forms are more frequently observed only at elevated firing temperatures. Da et al. (2021a) systematically demonstrated that the addition of CaF_2 promotes the formation of monoclinic and rhombohedral C_3S at comparatively lower clinkering temperatures. Importantly, this preferential appearance of high symmetry alite polymorphs is generally interpreted as arising from reduced kinetic barriers rather than from a fundamental shift in thermodynamic stability. Da et al. attributed this behavior to fluoride-induced lattice defects, enhanced ionic mobility, and early liquid-phase formation, which collectively facilitate atomic rearrangement during sintering and increase the kinetic accessibility of high-symmetry alite structures.

Earlier investigations into fluorine-bearing additives, including those by Boughanmi et al. (2018), provided foundational evidence that fluorine incorporation can induce lattice distortion and promote structural rearrangement in silicate phases, thereby influencing polymorphic development during clinkering. These early findings offer important historical context for later mechanistic interpretations based on CaF_2-assisted mineralization.

Representative examples of reported polymorph evolution and associated reductions in clinkering temperature for CaF_2-containing and co-doped systems are summarized in Table 1. These data highlight that both the extent of polymorph transformation and the magnitude of apparent temperature reduction are strongly system-dependent and influenced by raw-meal composition, co-dopants, and evaluation criteria (Laonamsai et al., 2025; Da et al., 2025).

Co-doping strategies further reinforce this kinetically driven interpretation. For example, ZnO–CaF_2 and CuO–CaF_2 systems have been shown to exhibit enhanced formation of high-symmetry alite polymorphs at reduced firing temperatures [36,39]. Such effects are commonly attributed to coupled anion–cation substitutions and melt-assisted diffusion processes that further lower kinetic constraints on polymorphic transformation. Collectively, available evidence suggests that polymorph evolution in CaF_2-containing systems is governed primarily by kinetic accessibility under defect- and melt-rich conditions, while thermodynamic factors appear to play a secondary role.

3 Co-doping synergies

Beyond its individual mineralizing effect, CaF_2 exhibits pronounced synergistic behavior when combined with selected metal oxides, resulting in further reductions in clinkering temperature and enhanced clinker reactivity. These co-doping systems operate through complementary mechanisms, in which CaF_2 primarily modifies lattice defect chemistry and melt-phase properties, while metal oxides influence cation mobility, intermediate phase formation, and polymorph stability. The synergistic effect of CaF_2 and TiO_2 has been widely reported in both laboratory and industrial clinker systems. Da et al. (2021a) demonstrated that TiO_2 promotes early formation of reactive aluminate and silicate intermediates and accelerates $CaCO_3$ decomposition, thereby lowering the overall sintering temperature. When combined with CaF_2, these effects are significantly intensified due to the simultaneous reduction in melt viscosity and enhancement of lattice-level diffusion. The dual action of TiO_2-induced lattice distortion and CaF_2-driven melt formation widens the effective formation window of alite, enabling clinker formation at temperatures below 1300 °C.

Copper oxide also exhibits strong synergy with CaF_2. Laonamsai et al. (2025) reported that CuO enhances CaO mobility and promotes the early formation of intermediate phases, while CaF_2 facilitates melt formation and stabilizes alite at reduced temperatures. X-ray photoelectron spectroscopy analysis revealed that fluorine predominantly substitutes for oxygen in silicate lattices, whereas Cu^{2+} preferentially substitutes for Fe^{3+} in ferrite phases. This coupled anion cation substitution induces simultaneous lattice distortion in both silicate and interstitial phases, markedly accelerating alite nucleation. As a result, substantial C_3S formation was achieved at temperatures as low as 1250 °C, which are insufficient for meaningful alite development in conventional systems.

Zinc oxide represents another effective co-dopant in CaF_2-based mineralization strategies. Da et al. (2025) demonstrated that ZnO and CaF_2 co-doping generates dual lattice defects through the concurrent substitution of Zn^{2+} into silicate phases and F^- into oxygen sites. This defect coupling significantly enhances

TABLE 1 Reported effects of CaF_2 and co-doped systems on clinkering temperature reduction.

Study/Year	System composition	CaF_2 dosage	Co-dopants	Temperature reduction (°C)	Key findings
Da et al., 2020	Ordinary Portland raw meal	1–3 wt%	None	50–100	CaF_2 accelerated $C_2S \rightarrow C_3S$ conversion and lowered melt temperature (Da et al., 2021b)
Dahhou et al., 2021	Belite-rich clinker	1–2 wt%	None	100–300	Early melt formation enabled major burnability enhancement (Dahhou et al., 2021)
Da et al., 2021	$C_3S + TiO_2$	1–3 wt%	TiO_2	50–150	Co-doping widened formation window and improved ionic mobility (Da et al., 2021a)
Laonamsai et al., 2025	$C_3S + CuO$	1–2 wt%	CuO	100–200	CuO enhanced CaO mobility while CaF_2 stabilized high-symmetry polymorphs (Laonamsai et al., 2025)
Da et al., 2025	$ZnO–CaF_2$ clinker	1–3 wt%	ZnO	100–200	Dual lattice defects enhanced burnability and polymorph stability (Da et al., 2025)
Mend et al., 2025	Fluorine-containing sludge	Equivalent 1–2 wt%	Zn, Cu, Fe impurities	50–150	Waste-derived CaF_2 maintained mineralizing effect and immobilized metals (Mend et al., 2025)
Xu et al., 2025	Fluorite tailings	~1 wt%	Fe, clay minerals	50–100	Multi-component synergy improved early and long-term strength (Xu et al., 2025)

Footnote: Reported clinkering temperature reductions are system- and criterion-dependent, reflecting combined effects of raw-meal composition, co-dopants, melt chemistry, processing conditions, and the criteria used to define clinker formation, rather than the isolated effect of CaF_2 alone.

phase transformation kinetics and promotes stabilization of the rhombohedral C_3S polymorph, as confirmed by characteristic X-ray diffraction peak shifts. In addition to improved burnability, $ZnO–CaF_2$ systems exhibit exceptionally low free-lime contents and efficient incorporation of zinc into clinker minerals, offering advantages for both clinker quality and heavy-metal immobilization.

Synergistic mineralization effects are particularly prominent in waste-derived CaF_2 systems, which inherently contain multiple co-dopants. Xu et al. (2025) reported that fluorite tailings containing CaF_2, iron oxides, and clay minerals produced strong multi-component mineralization effects, resulting in enhanced early- and long-term strength development despite compositional variability. Similarly, Da et al. (2022b) observed that fluorine-containing industrial sludges rich in CaF_2, MgF_2, and metal oxides generated cooperative lattice melt effects. Microstructural analysis revealed preferential fluorine enrichment at silicate grain boundaries, while Zn, Cu, and Ni were distributed across both silicate and interstitial phases, supporting a multi-scale synergy mechanism.

Collectively, these findings demonstrate that CaF_2-based co-doping systems operate through coordinated lattice-level, melt-phase, and polymorph-stabilization mechanisms. The presence of complementary metal oxides amplifies the mineralizing efficiency of CaF_2, enabling reliable low-temperature clinker formation across a wide range of raw-meal compositions. Such synergistic behavior is particularly advantageous for industrial applications involving waste-derived mineralizers, where compositional variability necessitates robust and adaptable mineralization strategies.

4 Industrial and environmental significance

The practical significance of CaF_2-based mineralization extends well beyond laboratory-scale studies and demonstrates strong

TABLE 2 Key knowledge gaps and research priorities for CaF_2-based mineralization.

Knowledge gap	Description of uncertainty	Suggested research direction
Relative contribution of lattice vs. melt mechanisms	Experimental studies do not isolate mechanism dominance	*In-situ* high-temperature XRD/synchrotron real-time phase tracking
Multi-component flux interaction (CaF_2 + metal oxides)	Synergy vs. antagonism unclear under variable oxide ratios	CALPHAD + molecular dynamics simulations to map eutectic behavior
Hydration inhibition threshold	Excess F may form insoluble CaF_2 layers, but critical limits unknown	Long-term hydration, pore solution chemistry and surface spectroscopy
Fluorine volatility and emissions	HF/SiF_4 formation risk poorly documented at kiln scale	Gas-phase capture studies, emission modeling, real-kiln monitoring
Leaching stability of doped clinkers	Long-term heavy metal stability uncertain under aggressive conditions	Accelerated aging + toxic leachability testing
Process control for variable waste streams	CaF_2 waste composition fluctuates → burnability instability	AI-enabled dosing adjustment, predictive thermodynamic feedback models
Impurity co-incorporation pathways	Role of Cu, Zn, Fe substitutions on C_3S stability incomplete	Atom probe tomography or nano-XRD studies on doped interface structures

potential for industrial implementation. Reducing the clinkering temperature through CaF_2 addition offers multiple operational advantages for cement manufacturing. Holban et al. (2015) reported that a reduction of 100 °C in kiln temperature can decrease thermal energy consumption by approximately 7%–12%, resulting in lower fuel costs and extended service life of refractory linings. Owing to its ability to promote early liquid-phase formation, CaF_2 also enables a reduction in residence time within the sintering zone without compromising clinker phase development, as demonstrated by Da et al. (2021b). This characteristic makes CaF_2-compatible mineralization strategies suitable for both wet and dry kiln technologies currently employed in commercial cement plants. Waste-derived mineralizers are of particular interest from a circular-economy perspective. Mend et al. (2025) demonstrated that fluorine-containing industrial sludge rich in CaF_2 and MgF_2 retains mineralizing performance comparable to that of natural fluorite and can partially replace virgin mineral resources. Similarly, Zhao et al. (2025) reported that low-temperature calcination of fluorine-rich sludge produces reactive fluoride phases that improve melt fluidity and facilitate the immobilization of hazardous elements during clinker formation. The ability of CaF_2 to incorporate heavy metals into silicate and aluminate clinker phases provides a significant environmental advantage, particularly for the co-processing of wastes containing fluorine, zinc, and copper.

Xu et al. (2025) showed that fluorite tailings containing CaF_2, iron oxides, and clay minerals, when used as co-dopants in high-silica clinker systems, enhance mechanical strength while ensuring stable incorporation of fluorine into clinker phases. These findings suggest that industrial by-products containing CaF_2, ZnO, Fe oxides, or Cu-bearing compounds should be regarded not as contaminants but as synergistic mineralizers. Da et al. (2022a) further emphasized that fluorine-containing sludge exhibits multi-component fluxing effects, enabling reliable reductions in clinkering temperature even under variable raw-meal compositions a critical requirement for industrial-scale applications. When applied at optimized dosages of 1–3 wt%, CaF_2-based mineralization consistently improves clinker burnability, reduces free-lime content, lowers CO_2 emissions, and enhances the immobilization of trace metals within clinker minerals. Consequently, CaF_2-based mineralization represents a practical, resource-efficient, and environmentally beneficial strategy for achieving low-temperature, energy-efficient, and low-carbon cement production.

5 Knowledge gaps and future directions

Despite growing evidence supporting CaF_2-based mineralization, several unresolved issues remain that limit predictive control and large-scale industrial implementation. The key knowledge gaps and corresponding research priorities are summarized in Table 2. A major limitation lies in the lack of quantitative separation between lattice-level defect formation and melt-phase enhancement under realistic clinkering conditions. Addressing this issue will require *in-situ* high-temperature techniques, such as synchrotron X-ray diffraction and real-time phase tracking, to directly observe defect evolution and phase transformations. Additional challenges arise in multi-component systems derived from industrial wastes, where interactions among CaF_2, metal oxides, and melt structure remain insufficiently understood.

Predictive thermodynamic frameworks combining CALPHAD-based modeling with molecular dynamics simulations are needed to reliably describe eutectic behavior, phase equilibria, and fluxing efficiency in such complex systems. Hydration performance represents another critical uncertainty. Excessive fluorine may lead to the formation of CaF_2-rich surface layers that delay early hydration, yet composition-specific threshold levels remain poorly defined. Long-term hydration studies incorporating pore-solution chemistry and surface-spectroscopic analysis are therefore required to establish safe operational windows. Finally, environmental and process-control considerations including fluorine volatility, long-term leaching stability of immobilized metals, and variability in waste-derived feedstocks require systematic investigation. Comprehensive emission monitoring accelerated leaching tests, and adaptive process-control strategies will be essential to ensure environmentally compliant and robust low-temperature clinker production.

6 Conclusion

Calcium fluoride (CaF_2) is one of the most effective mineralizers for reducing the clinkering temperature of Portland cement and represents a practical pathway toward low-carbon cement production. This mini review highlights that the mineralizing action of CaF_2 arises from the combined effects of fluoride-induced lattice defect formation, melt-phase modification, and stabilization of high-symmetry alite polymorphs. Fluoride substitution in the C_3S lattice generates calcium vacancies that enhance ionic mobility and lower the activation energy for the C_2S-to-C_3S transformation, while simultaneous reductions in liquidus temperature and melt viscosity promote early liquid-phase formation and accelerated clinker reactions. Together, these mechanisms enable efficient clinker formation at temperatures 50 °C–300 °C below conventional conditions.

The mineralizing efficiency of CaF_2 is further amplified through synergistic interactions with metal oxides such as TiO_2, CuO, and ZnO, which enhance lattice distortion, melt fluidity, and polymorph stability. Importantly, CaF_2 derived from industrial waste streams exhibits mineralizing performance comparable to that of natural fluorite, while facilitating the immobilization of fluorine and heavy metals within clinker phases. When applied at optimized dosages of 1–3 wt%, CaF_2-based mineralization consistently reduces energy consumption and CO_2 emissions while improving clinker burnability and process robustness. Overall, CaF_2-based mineralization offers a viable, resource-efficient, and environmentally beneficial strategy for low-temperature clinker production. Continued advances in mechanistic understanding, thermodynamic modeling, and process control will further support its industrial implementation in next-generation sustainable cement manufacturing.

Author contributions

BM: Conceptualization, Writing – original draft, Writing – review and editing. YL: Formal Analysis, Writing – review and editing. D-YK: Methodology, Writing – review and editing. J-HK: Supervision, Validation, Writing – review and editing. Y-SC: Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review and editing.

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Conflict of interest

The author(s) declared that this work was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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