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Fractal morphology-governed structural build-up in reactive particulate suspensions: insights from tricalcium silicate hydration

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Abstract: Structure formation in reactive particulate suspensions is governed by the coupled evolution of particle connectivity, interfacial growth, and multiscale morphology. This study applies a modeling framework that integrates boundary nucleation and growth (BNG) kinetics with a fractal-based hydrate-bridging model for tricalcium silicate (C_3S) pastes. The framework describes the evolution of structural build-up measured by slow penetration tests and small-amplitude oscillatory shear (SAOS) across different water-to-solid ratios and calcium nitrate dosages. A fitted fractal-related parameter, β , is used as a model-derived descriptor of hydrate morphology and internal connectivity. The trends in β are corroborated by observations from scanning electron microscopy (SEM), dynamic light scattering (DLS), and ^1H nuclear magnetic resonance (NMR). In calcium nitrate-modified systems, the reduced hydrate size is consistent with

classical dissolution-precipitation theory. At comparable hydration levels, β shows a positive correlation with T_2 relaxation time differences, suggesting that hydrate morphology influences pore filling. The temporal evolution of β , showing initial simplification followed by re-complexification, is consistent with Monte Carlo simulations. These results provide a physically informed interpretation of the link between hydrate-scale structural evolution and early-age rheological behavior within the proposed modeling framework.

Keywords: Reactive particulate suspensions; Fractal growth; Structure-property relationships; Hydrate connectivity

1 Introduction:

The hydration of cementitious materials represents a complex multiscale process in which chemical reactions, phase transformations, particle interactions, and microstructural evolution occur simultaneously across a wide range of time and length scales [1–3]. As hydration proceeds, reactive cementitious suspensions gradually develop a heterogeneous microstructure composed of unreacted particles, newly formed hydration products, and an evolving pore network [2,4]. This early-age microstructure governs the formation of interparticle connections and therefore strongly influences rheological properties, structural build-up, and the subsequent development of mechanical performance [5–7]. Establishing a quantitative link between hydration-driven microstructure evolution and macroscopic structural response therefore requires not only experimental characterization, but also physically informed modelling capable of capturing morphology, connectivity, and structure-property relationships.

As a representative reactive mineral phase in cementitious systems, tricalcium silicate (C_3S) provides an ideal model system for investigating hydration-driven microstructural evolution and structural build-up. [7,8]. During hydration, C_3S reacts with water to form calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). Unlike crystalline products, the C-S-H generated from C_3S hydration is predominantly X-ray amorphous to low-crystalline due to the rapid reaction kinetics, high supersaturation,

and severe diffusion limitations during early hydration [9–12]. From a thermodynamic perspective, although crystalline phases are energetically more favorable [13,14], systems often remain in metastable states, for example where atomic rearrangement is insufficient for long-range order [9,15,16]. It can be inferred that the aggregation of low-crystalline C-S-H phases, from nanoscale clusters to larger assemblies, leads to the development of connectivity within the hydrate structure, which governs early-age properties. This connectivity is distinct from the flocculated network of cement grains and instead reflects the evolving links formed between hydration products at a smaller scale. Therefore, accurately characterizing and understanding their disordered growth in space and time is key to linking microstructural evolution with early-age mechanical properties.

Numerous studies have investigated the evolution of structural build-up during hydration by linking it to hydration kinetics, pore structure development, and microstructural changes [7,17–23]. In particular, Tattersall and Banfill [24] established a fundamental understanding of yield stress evolution and structural build-up throughout the fresh state, from water addition to initial setting. Roussel [25] introduced later a widely adopted thixotropy model relating microstructural evolution to time-dependent increases in yield stress. Sant et al. [26] further explored the connection between early hydration and rheological properties by directly linking microstructural formation to yield stress development in cement pastes. A representative modeling framework, the Yodel model [27], relates solid volume fraction and particle interactions to yield stress behavior. It has been extended in later works to incorporate hydration sensitivity and interparticle force refinements for improved early-age predictions [28–30]. Perrot et al. developed a model predicting the transition of structural build-up from linear to exponential evolution [31]. Additionally, Miranda et al. [32] developed a hydration-based model to capture early-age viscosity changes, while Navarrete et al. [33] introduced a polynomial regression model to predict structural build-up across varying mix designs. Recent work by Michel et al. [34] has shown that grain-to-grain contact geometry plays a critical role in structural build-up, indicating that the location and morphology of hydration products at particle contacts are key factors governing

early stiffening. Despite these advances, many existing models still rely on idealized assumptions and insufficiently account for the evolving quantity, morphology, and complexity of hydration products across multiple scales [35].

To address the complex and disordered nature of early-age microstructural development or the growth of hydration products, stochastic modeling approaches such as Monte Carlo simulations and fractal theory have been increasingly employed in cement hydration studies [36–41]. Monte Carlo simulations have been used to model mesoscale hydration processes and pore structure evolution [42], investigate the aggregation behavior of C-S-H phases influenced by surface charge [43], and simulate the formation of nano-granular textures in cement hydrates along with their mechanical implications [44]. These stochastic approaches offer powerful tools for capturing the inherent randomness of nucleation, growth, and aggregation at the nano particle scale, providing valuable insights into the spatial heterogeneity and evolving complexity of hydration products. Building on these insights, our previous study [35] established a hydrate-bridging-based yield stress model, incorporating Monte Carlo-derived relations between hydrate size and amount to capture early-age structural build-up.

In this study, we apply a fractal-based hydrate-bridging model to quantify the structural evolution and early-age structural build-up of C_3S suspensions during hydration. The framework couples heat release data with boundary nucleation and growth (BNG) kinetics to obtain the transformed volume fraction of hydration products, which is then used as input for the hydrate-bridging model. The predicted structural responses are evaluated against slow penetration resistance tests and small-amplitude oscillatory shear (SAOS) measurements. To establish a microstructure-property link, the fitted morphology-related parameter is further analyzed together with low-field nuclear magnetic resonance (LF-NMR), dynamic light scattering (DLS), and scanning electron microscopy (SEM) results. Particular attention is paid to the relationship between the fractal parameter, hydrate morphology, pore filling behavior, and structural build-up at comparable hydration levels. In addition, Monte Carlo simulations and fractal theory are used to interpret the temporal evolution of the fitted parameter, providing insight into the dynamic development of hydrate connectivity and

microstructural complexity during early hydration.

2 Materials and experiments

2.1 Materials

The tricalcium silicate (C_3S , M2 type) used in this study was purchased from Hunan Keyan Shu Technology Service Co., Ltd. Its XRD pattern is provided in the **Supplementary materials** (Fig. S1). The Blaine surface and bulk density of the C_3S powder are $2710 \text{ cm}^2/\text{g}$ (S_A) and 3.16 g/cm^3 , respectively. The particle size distribution of C_3S was measured using a laser diffraction analyzer (Malvern Mastersizer S). Isopropanol (IPA) and water were used as the dispersant to determine the reference PSD of the unhydrated C_3S powder, following proposed standard procedures for laser diffraction measurements of cement powders [45]. Both results are shown in Fig. 1. Accordingly, the IPA-based result is adopted as the reference PSD of the unhydrated powder, while the water-based result is regarded as the condition-affected apparent particle size distribution in aqueous environments. For the water-based measurement, the particle sizes corresponding to d_{10} , d_{50} , and d_{90} are $1.93 \text{ }\mu\text{m}$, $15.55 \text{ }\mu\text{m}$, and $40.65 \text{ }\mu\text{m}$, respectively. For the IPA-based measurement, the corresponding d_{10} , d_{50} , and d_{90} values are $5.22 \text{ }\mu\text{m}$, $12.89 \text{ }\mu\text{m}$, and $32.45 \text{ }\mu\text{m}$, respectively.

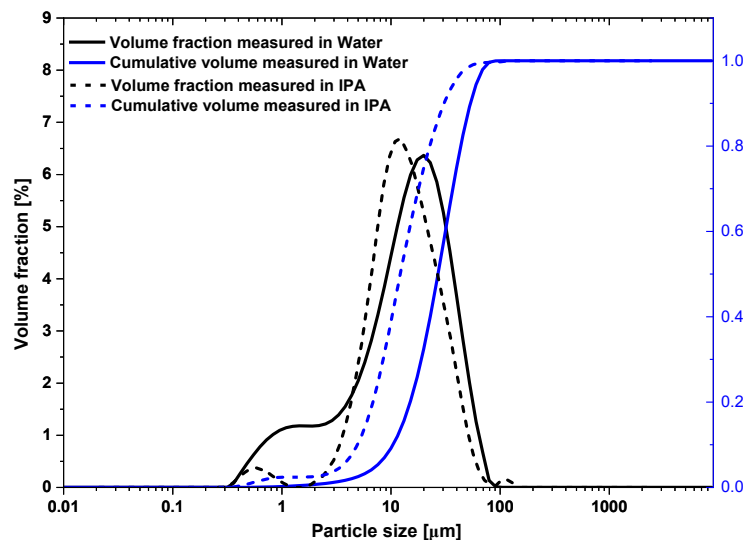


Fig. 1 Particle size distribution of C_3S powders measured by laser diffraction with isopropanol (IPA) and water as dispersants. The IPA test result is taken as the reference particle size distribution of unhydrated C_3S , whereas the water test reflects

the apparent PSD in an aqueous environment.

Water-to- C_3S powder ratios ranging from 0.32 to 0.40 were adopted, corresponding to the samples denoted as C_3S032 , C_3S036 and C_3S040 . Calcium nitrate was introduced at dosages of 0, 3.0 and 6.0 wt.% by mass of C_3S . Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, purity of 99 %, Carl Roth GmbH) was utilized, and the extra water introduced by the hydrate salt was subtracted from the mixing water to maintain the designed water-to- C_3S ratio. These mixtures were prepared at a constant water-to- C_3S ratio of 0.40 and labeled $C_3S040(REF)$, $C_3S040D3$ and $C_3S040D6$, respectively. For sample preparation, the pre-weighed C_3S powder was slowly added to deionized water and manually stirred for 1 min to achieve full pre-wetting and avoid splashing. The paste was then mechanically vibrated for another 1 min at a constant frequency to ensure consistent mixing. The same mixing procedure was applied to all samples.

2.2 Experiments

2.2.1 Slow Penetration Test

The penetration test was performed using the ToniSET Force apparatus (Toni Technik-Baustoffprüfsysteme GmbH, Germany). Detailed information on the device is available in Refs [35,46]. Approx. 20 g of paste was filled into a cylindrical holder and sealed with a plastic cover to prevent evaporation. Before testing, a steel penetrator with a cylindrical-conical geometry ($h_1 = 6$ mm, $h_2 = 8.5$ mm, $2R = 6$ mm,) was embedded into the paste to ensure full submersion and create an overhead cavity, maintaining a consistent friction surface. The penetrator sank vertically at a constant rate of 0.01 mm/min, and the penetration force is continuously recorded as a function of time. The measurement ended when the force reached 400 N or the time limit of 480 min. The penetrator geometry (including the sample holder) and displacement-time data are shown in Fig. 2. According to the equation from Lootens et al. [47], the static yield stress can be calculated as follows:

$$\tau_0 = \frac{F}{\pi R \sqrt{R^2 + h_2^2} + 2\pi R h_1} \quad (1)$$

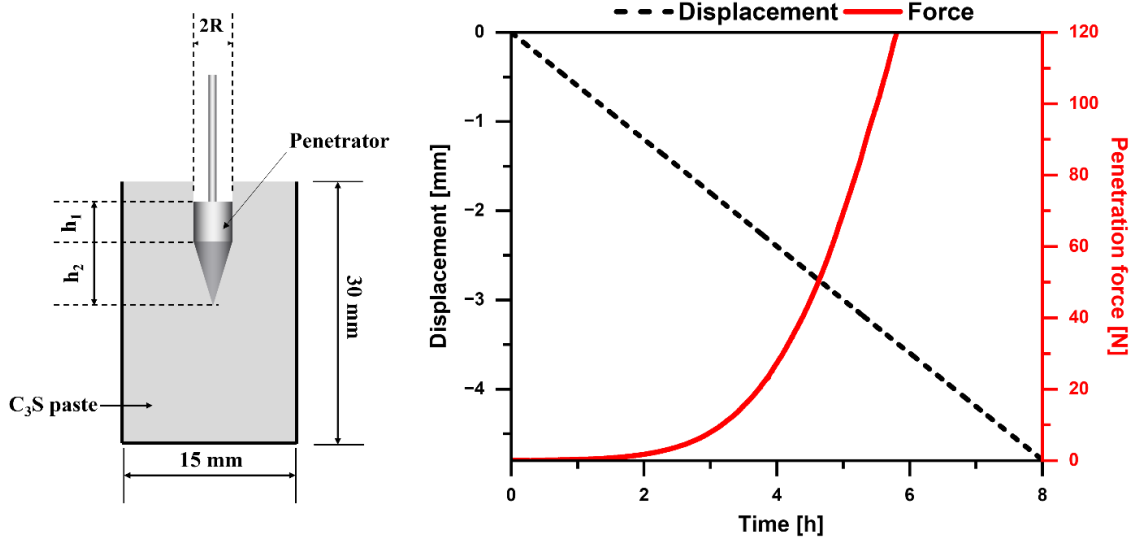


Fig. 2 Dimensions of the sample and the penetrator, along with a representative example of displacement and force as functions of time.

The penetration measurement is highly sensitive to temperature. Therefore, raw material storage, sample preparation, and penetration testing were all conducted at 20 °C.

2.2.2 Small amplitude oscillatory shear test (SAOS)

Small amplitude oscillatory shear (SAOS) tests were conducted using an Anton Paar MCR 502 WESP rheometer fitted with a 25 mm diameter parallel-plate geometry. To suppress water evaporation during the 6-hour SAOS measurement, a solvent trap was employed, and the test temperature was controlled at 20 °C with a plate gap of 1 mm. All measurements were carried out at a fixed frequency of 1 Hz, a typical frequency adopted for cement-based materials [48,49]. Prior to the SAOS time sweep measurements, preliminary checks were conducted to select a small strain amplitude within the linear viscoelastic region. A typical strain amplitude of 10^{-5} was used for the subsequent time sweep tests to minimize disturbance to the evolving structure [23]. The time-dependent structural build-up was characterized by the relative storage modulus, $\Delta G'$, calculated by subtracting the initial storage modulus from the measured value. All tests were repeated in triplicate. For each test, 5 g of pure C₃S powder was mixed with a designed amount of water and chemical admixture following the mixing protocol described in Section 2.1. Immediately after mixing, the fresh sample was

loaded onto the rheometer, for the 6 h SAOS time sweep test.

2.2.3 Low-field NMR

Low-field ^1H NMR was employed to monitor the microstructural evolution of C_3S paste by analyzing the transverse relaxation time (T_2) distribution. The measurements were performed using a VTMR20-010 V-I spectrometer (Niumag, Suzhou, China) operating at 0.5 T, with a field homogeneity deviation below 30 ppm and a stability drift below 200 Hz/h. The 90° and 180° RF pulse lengths were 3.12 μs and 5.20 μs , respectively. The Carr-Purcell-Meiboom-Gill (CPMG) sequence was employed due to its short measurement duration, with an echo time of 0.08 ms, 4000 echoes, and 64 scans.

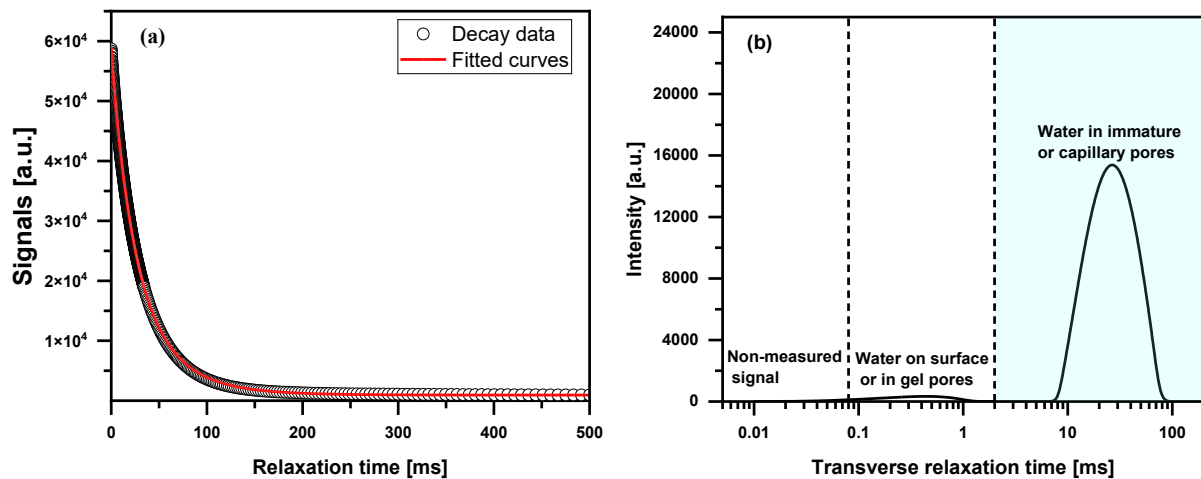


Fig. 3 Decay data as a function of relaxation time (a) and a typical transverse relaxation time distribution (b). In subplot (b), the first dashed line (from the left) indicates the echo time of 0.08 ms, and the second dashed line marks 2 ms.

Approx. 2 g of freshly prepared paste was placed into a hydrogen-free tube and sealed to prevent evaporation. To avoid sample disturbance, vibration was minimized during transfer to the NMR instrument. Using the CPMG sequence, decay curves were obtained (Fig. 3a), and T_2 distributions from 10 min to 24 h were calculated with the built-in Niumag software, using the simultaneous iterative reconstruction technique (SIRT). A representative T_2 distribution is shown in Fig. 3b, displaying two peaks: one corresponding to surface-adsorbed or gel pore water (designated as $T_{2,G}$, with $T_2 < 2$ ms), and another associated with water in immature or capillary pores (designated as $T_{2,P}$, ranging from 5-100 ms), consistent with previous studies [50–52]. It is noted that

the signals below the echo time result from calculated or inverted data, which are indicated as non-measurable signals in Fig. 3b. The intensity-weighted T_2 value of peaks ($\overline{T_2}$) was calculated from the discrete data according to Eq. (2):

$$\overline{T_2} = \left(\sum_{i=1}^n I_i \right)^{-1} \cdot \sum_{i=1}^n T_{2,i} \cdot I_i \quad (2)$$

where $T_{2,i}$ is the transverse relaxation time of the i th measured data, I_i is the corresponding signal intensity (or integral area), and n is the total amount of data. This study focuses on the peak from immature pores, as it exhibits higher signal intensity and more directly reflects changes in interparticle spacing and filling of hydrates in pores during early hydration.

2.2.4 Isothermal calorimetry

Isothermal calorimetric tests were conducted using a TAM AIR calorimeter (TA Instruments, New Castle, DE, USA) to monitor heat release during C₃S hydration at 20 °C. Quartz sand was used as the reference for the measurement. Heat flow was recorded every 60 s for 72 h. Each measurement was repeated three times to minimize experimental errors.

2.2.5 Dynamic light scattering

To assess hydrate-related nanoparticle size during hydration, dynamic light scattering (DLS) measurements were conducted on the filtered suspension obtained from C₃S pastes after hydration stopping with IPA. The detected nanoparticles are mainly associated with nanoscale hydration products such as C-S-H and possibly portlandite. A DLS instrument (Zetasizer Malvern Instruments Ltd., UK) with a 173° detector angle was used. Isopropanol (IPA), with a molecular size of approx. 0.52 nm (estimated from molecular structure), was used to stop hydration and to wash out the nano-hydrates from the samples. The C₃S paste was mixed with IPA at a 1:4 ratio, following the protocol described in Refs [35,53], and stirred for 2 min. After 15 min of settling, the supernatant was obtained and filtered through a 450 nm syringe filter to collect the solutions with hydrates. Care was taken to exclude any grains from the bottom, as their presence could lead to unacceptable results. Measurements were repeated five times for each sample.

2.2.6 Scanning electron microscope (SEM)

Hydration of C_3S was stopped at 4 h by solvent exchange with isopropanol, followed by drying at 40 °C until a constant weight was achieved. The microstructure of the resulting powder-like hydrated C_3S samples was examined using a scanning electron microscope (SEM; ZEISS GeminiSEM 500 NanoVP, Carl Zeiss Microscopy Deutschland GmbH, Germany) under a chamber pressure of 100 Pa and an accelerating voltage of 15 kV. Sample preparation followed the procedure outlined in Section 2.1. To minimize potential carbonation, the sample holder was covered with a thin film and stored in a nitrogen-filled environment prior to imaging.

3 Theoretical frameworks

The structural build-up of cement paste during early hydration is commonly governed by interparticle bridges formed by hydration products [54], including C_3S and C_3A reaction products such as C-S-H and ettringite (AFt). In this study, the structural response, $S(t)$, is used as a general descriptor of build-up and may be represented experimentally by either the increase in apparent static yield stress, $\Delta\tau_0$, obtained from slow penetration tests or the relative storage modulus, $\Delta G'$, obtained from SAOS time sweep tests. It is assumed that $S(t)$ scales with the local interparticle bridging force F_{int} :

$$S(t) \propto F_{\text{int}} \quad (3)$$

The formation of physical connections between particles, particularly through hydrate bridges, is considered critical in governing the early development of mechanical properties in fresh paste [35]. These bridges, typically C-S-H phases, form within interstitial spaces between particles and serve as the foundational network contributing to structural build-up. The F_{int} is assumed to scale with the probability of bridge formation, P , which relates to the characteristic size of bridging hydrates and the characteristic interparticle separation:

$$F_{\text{int}} \propto P \propto \frac{\varepsilon_L}{h} \quad (\varepsilon_L \geq 0) \quad (4)$$

where ε_L is the characteristic size of bridging hydrates, and h represents the characteristic interparticle separation. According to Eq. 4, interparticle bridging is

promoted by larger hydrate bridges or shorter particle separation. Therefore, the following sections quantify the representative interparticle spacing, establish the fractal scaling relationship for hydrate growth, and couple these terms with hydration kinetics to describe $S(t)$.

3.1 Representative interparticle spacing for the bridging model

The definition of interparticle spacing is not unique and depends on the underlying physical considerations. In this study, several spacing descriptors are considered, including the mean interparticle distance H_s [55], the water-film thickness H_w , the void-based characteristic spacing H_v , and the nanoscale separation H_k . These spacing measures correspond to different physical scales, ranging from nanoscale separation at particle contacts to microscale structural spacing governed by solid content and particle packing. Among these, the mean interparticle distance H_s , defined as:

$$H_s = d_0 \left(\left(\frac{\phi_{\max}}{\phi} \right)^{1/3} - 1 \right) \quad (5)$$

where d_0 is the initial particle size of C_3S powder, approximated by the median particle diameter d_{50} obtained from laser diffraction measurements, ϕ is the solid content and $\phi_{\max}$ the maximum solid content (lubricated packing limit) and was estimated using empirical correlations that incorporate the particle size distribution, specifically d_{10} and d_{90} [56,57].

The water film thickness H_w was introduced following the concept proposed by Kwan and co-workers [58,59], in which the effects of water content, packing density and solid surface area on fresh cementitious systems are evaluated through the excess water layer coating the solid particles. The water film thickness H_w is defined as the average surface-to-surface separation formed by the excess water coating the solid particles (i.e., cement and aggregate). It can be expressed as the ratio between the excess water volume and the total solid surface area:

$$H_w = \frac{2V_{\text{ex}}}{A_s} \quad (6)$$

where V_{ex} is the excess water volume and A_s is the total surface area of solid particles.

The factor of 2 accounts for the surface-to-surface separation between adjacent particles. The excess water volume is obtained by subtracting the water required to fill the voids at maximum packing from the total water content. Expressed in terms of solid volume fraction, it can be written as:

$$V_{\text{ex}} = \frac{1-\phi}{\phi} - \frac{1-\phi_{\text{max}}}{\phi_{\text{max}}} \quad (7)$$

Substituting the above expressions into the definition yields:

$$H_w = \frac{2}{A_s} \left[\frac{1-\phi}{\phi} - \frac{1-\phi_{\text{max}}}{\phi_{\text{max}}} \right] \quad (8)$$

Compared to H_w , which is controlled by excess water, H_v is purely governed by geometric packing and void structure. The void-based spacing H_v was estimated from the hydraulic-radius concept [60], where the spacing is defined as the ratio between void volume and solid surface area.

$$H_v = \frac{V_{\text{void}}}{A_s} \quad (9)$$

For approximately spherical particles [61], this gives:

$$H_v = \frac{d_0}{6} \left[\frac{1-\phi}{\phi} \right] \quad (10)$$

The Kapur-type distance H_k is introduced as an equivalent interparticle separation associated with interaction forces. Following the formulation reported by Flatt and Bowen [27], which was based on the work of Kapur et al. [62], it is expressed as:

$$H_k = h_0 [9.5 \exp(-4.5\phi)] \quad (11)$$

where h_0 is the closest distance of approach between particles, taken as 5.5 Å according to Ref. [62]. The relationships between H_s and the other spacing parameters were analyzed. As shown in Fig. 4, the spacing descriptors H_w , H_v , and H_k exhibit strong linear correlations with the mean interparticle distance H_s , with R^2 values of approximately 0.99. Although these descriptors represent different physical scales, they are primarily governed by the solid volume fraction within the investigated range. The strong correlation between H_k and H_s suggests that the nanoscale contact-related separation follows the same monotonic evolution as the mean geometrical spacing.

Therefore, using H_s in the bridging probability model does not imply that contact-scale separation is neglected, nor does it assume that H_s is identical to the minimum contact-point distance. Instead, H_s is adopted as an effective representative spacing parameter that captures the solid-volume-fraction-controlled evolution of particle separation across different spacing regimes.

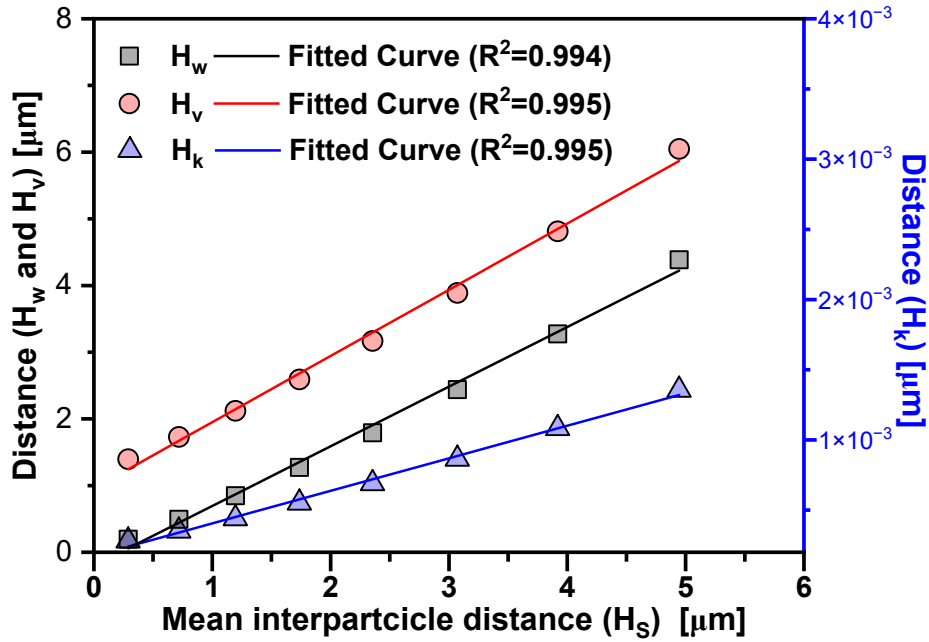


Fig. 4 Correlation between the mean interparticle distance H_s and different characteristic spacing parameters, including the water film thickness H_w , void-based spacing H_v , and Kapur-type interaction distance H_k . The solid volume fraction varied from 0.30 to 0.65 as input.

3.2 Fractal growth of bridging hydrates based on Monte Carlo simulations

To quantify the size parameter ε_L of bridging hydrates, a fractal-based framework was used, assuming that C-S-H gels grow through a reaction-limited aggregation (RLA) mechanism. This assumption is supported by kinetic Monte Carlo simulations showing that early-age hydration is governed by the RLA of nanoscale precursors [63], leading to a rapid increase in reactive surface area. The nanoscale building blocks can be understood as thermodynamically stable prenucleation clusters (PNCs) or, more broadly, as metastable primary particles (PPs), typically represented by monomers such as Ca^{2+} , $\text{SiO}_2(\text{OH})_2^{2-}$, or their combination $\text{CaSiO}_2(\text{OH})_2$ [64–66]. The characteristic size parameter of bridging hydrates, ε_L , was assumed to scale with the

average cluster height H_B , which follows a fractal scaling relationship with particle number N :

$$\varepsilon_L \propto H_B \propto N^{\frac{1}{D_B - d_s}} \quad (12)$$

where D_B is the fractal dimension of the cluster and d_s is the dimension of the nucleation sites, taken as 2. In this study, Monte Carlo simulations were employed as an analogy for hydrate growth along particle boundaries. The simulation was initialized with a line of length Unit, set as either 250 or 500. Particles were then generated 1.0 unit vertically above this line and allowed to move randomly. Once a particle contacts the line or an already attached particle, it adheres to the cluster with a sticking probability K (i.e., 0.2 or 1). The simulation MATLAB codes have been made available on GitHub (<https://github.com/yanliangji0820/Monte-carlo-hydrate-growth.git>). Fig. 5 presents the simulation results for cluster growth under different particle geometries and simulation conditions.

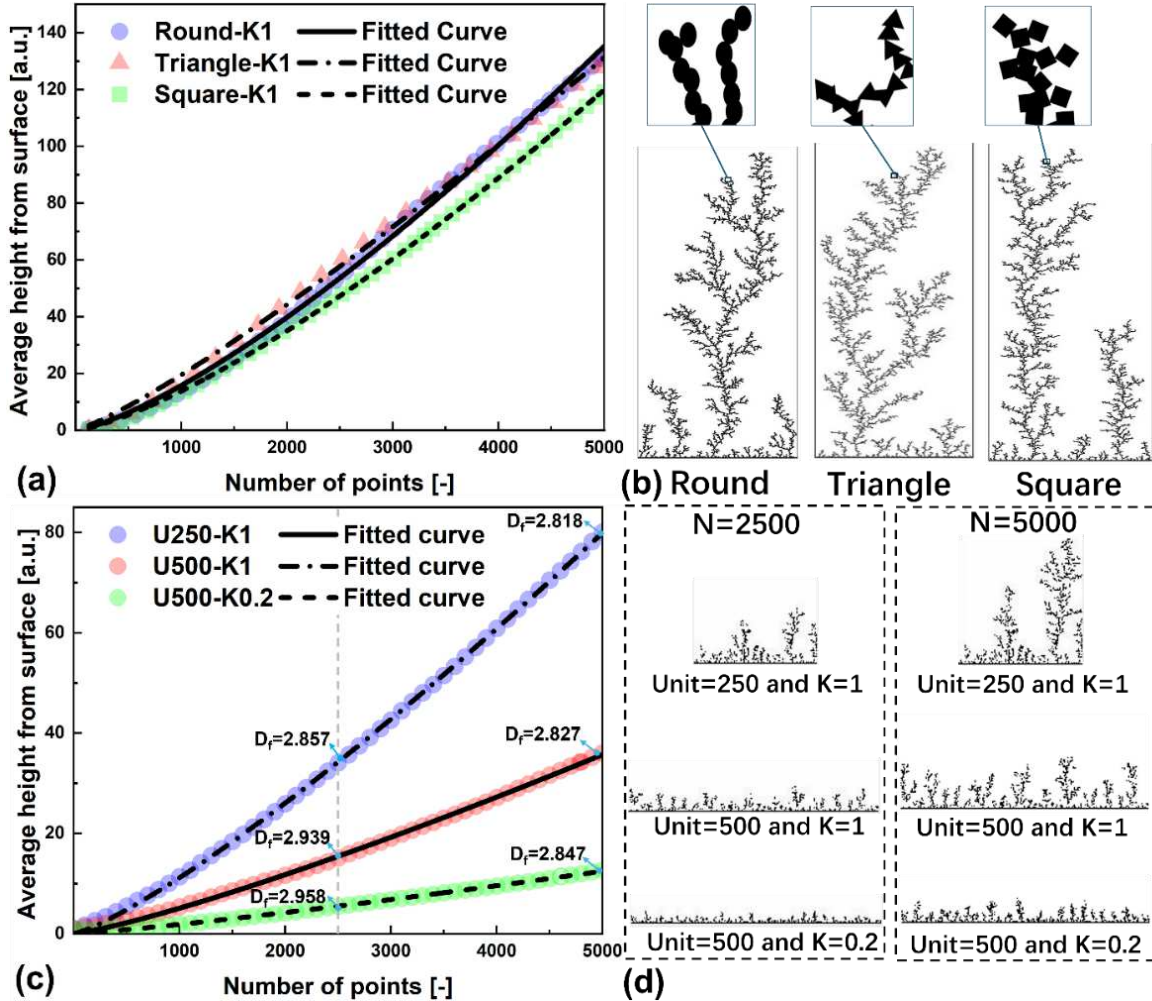


Fig. 5 Average cluster height as a function of particle number for different particle shapes (a) and the corresponding morphologies at 5000 particles (b). The particle shapes are circular, triangular, and square ($K = 1$). The height scale in (a, b) is larger than that in the unit-based simulations because extended geometrical particles are used. Average cluster height for different simulation parameters (c) and the corresponding morphologies at 5000 particles (d). From top to bottom: Unit = 250, $K = 1$; Unit = 500, $K = 1$; and Unit = 500, $K = 0.2$.

Figs. 5a and 5b show the effect of particle shape under equal-area conditions. It is found that circular, triangular, and square particles all follow the scaling relation given by Eq. 12. Importantly, square particles form the most compact and continuous clusters, resulting in the lowest normalized height for a given particle number. Triangular and circular particles exhibit more open structures and higher normalized heights under the same conditions. Figs. 5c and 5d further show the effects of particle number, boundary length, and sticking probability on the fractal growth process. The fitted results indicate that: i) the fitted fractal dimension D_B decreases with increasing particle number; ii) a larger boundary length leads to a higher D_B , suggesting more compact and complex clusters; and iii) a higher sticking probability results in a lower D_B , suggesting simpler cluster structures. These results support the use of Eq. 12 to link the number of hydration-product units to the characteristic bridge size in the proposed structural build-up model.

3.3 Hydration-driven structural build-up model

To couple hydration kinetics with structural build-up, the BNG model was first used to quantify the transformed volume fraction of hydration products, $X_T(t)$, from calorimetric data. The measured heat flow is related to the transformation rate as:

$$Q(t) = \frac{AdX_T(t)}{dt} \quad (13)$$

where A is a scaling factor between the calculated transformation rate and the measured heat flow. The transformed volume fraction, $X_T(t)$, is then used as the kinetic input for the hydrate-bridging model. The effective number of hydration product units contributing to bridge formation is assumed to be proportional to $X_T(t)$:

$$N_h(t) = N_0 X_T(t) \quad (14)$$

In Eq. 14, $N_h(t)$ is the effective number of hydration product units and N_0 is a proportionality constant. Assuming fractal growth of bridging hydrates, the characteristic size parameter of bridging hydrates can be written as:

$$\varepsilon_L(t) = \varepsilon_0 [X_T(t)]^{\beta/2} \quad (15)$$

where $\varepsilon_L(t)$ is the characteristic size parameter of bridging hydrates, and β is a morphology-related scaling exponent. As discussed in Section 3.1, h can be represented by H_s , which contains information about particle spacings at different scales due to their linear correlation (Fig. 4). The bridging probability is then expressed as:

$$P_b(t) \propto \frac{\varepsilon_L(t)}{H_s} \quad (16)$$

where $P_b(t)$ is the bridging probability. Accordingly, the structural response $S(t)$, represented experimentally by $\Delta\tau_0$ from penetration tests or by $\Delta G'$ from SAOS time sweep tests, can be written as:

$$S(t) = \frac{\alpha [X_T(t)]^{\frac{\beta}{2}}}{H_s} \quad (17)$$

with

$$\beta = \frac{1}{D_s} + \frac{1}{D_B - 2} \quad (18)$$

where α is a proportionality coefficient relating bridge formation to structural response, and D_s and D_B represent the fractal dimensions of the cluster in pore space (defined in Ref. [35]) and on the surface boundary, respectively. In this formulation, $X_T(t)$ is obtained independently from calorimetry through the BNG model, while only α and β are fitted in the structural build-up model. The transformed volume fraction $X_T(t)$ is calculated using the BNG model:

$$X_T(t) = 1 - \exp \left(-2O_b \int_0^{G_t} (1 - \exp(-Y^e)) dy \right) \quad (19)$$

In Eq. 19,

$$Y^e = \frac{\pi I_B}{3} G^2 (t - t_0)^3 \left(1 - \frac{3y^2}{G^2 (t - t_0)^2} + \frac{2y^3}{G^3 (t - t_0)^3} \right) \quad (\text{for } t - t_0 > y/G) \quad (20)$$

$$Y^e = 0 \quad (\text{for } t - t_0 \leq y/G) \quad (21)$$

and,

$$O_b = \frac{S_A}{R_{wc} / \rho_w + 1 / \rho_c} \quad (22)$$

Here, R_{wc} is the water-to-cement ratio, and ρ_w and ρ_c are the densities of water and cement, respectively. The parameters G and I_B represent the linear growth rate of hydrates and the nucleation rate per unit boundary area, respectively, while O_b refers to the total boundary area per unit volume. Two additional parameters are introduced for fitting the calorimetric data: A , which converts the modeled transformation rate into the experimentally measured heat flow, and t_0 , which accounts for the delayed onset of nucleation. In the BNG fitting procedure, the four kinetic parameters G , I_B , t_0 , and A are optimized using the heat flow data. The resulting transformed volume fraction $X_T(t)$ is then used as the kinetic input for the hydrate-bridging model. In the subsequent structural build-up fitting, only α and β are optimized. All calculations were implemented using custom MATLAB code with parallel computing to improve numerical accuracy and computational efficiency. The BNG-derived $X_T(t)$ describes hydrate formation after the onset of nucleation. When $t < t_0$, the measured structural response shows only a minor increase, within 5% of the 6 h value. Therefore, this induction-stage response is not used for mechanistic interpretation. The hydrate-bridging model is applied only for $t \geq t_0$, and the fitted parameters α and β are interpreted for the post-nucleation regime, where hydration-product formation can be linked to the measured structural build-up.

4 Results and discussions

4.1 Isothermal calorimetry measurement and its fitting

Fig. 6 illustrates the heat flow and cumulative heat of C_3S pastes with varying

water-to-solid ratios ($w/s = 0.32, 0.36, 0.40$). In the heat flow plots, the experimental data are well fitted by the Boundary Nucleation and Growth (BNG) model (Eq. 19), capturing both the timing and shape of the main hydration peak. It should be noted that the BNG fitting is used here to quantify hydration progress and to provide kinetic input for the subsequent structural build-up model, rather than to directly define the rheologically relevant build-up window. The heat flow profiles show minimal variation across the different w/s ratios, with all peak values below 4 mW/g, and occurring at similar times. The cumulative heat curves overlap closely within the first 12 h, indicating similar early hydration behavior. Beyond 12 h, the paste with $w/s = 0.36$ exhibits slightly higher total heat release compared to the others, suggesting marginally more extended hydration. When comparing the time to reach 6 J/g of cumulative heat, all samples achieve this point within a narrow time window, with the $w/s = 0.36$ and 0.40 samples reaching it approx. 10 min earlier than the other. These results indicate that the influence of water content on hydration kinetics is limited during early stages but may become more apparent in later periods.

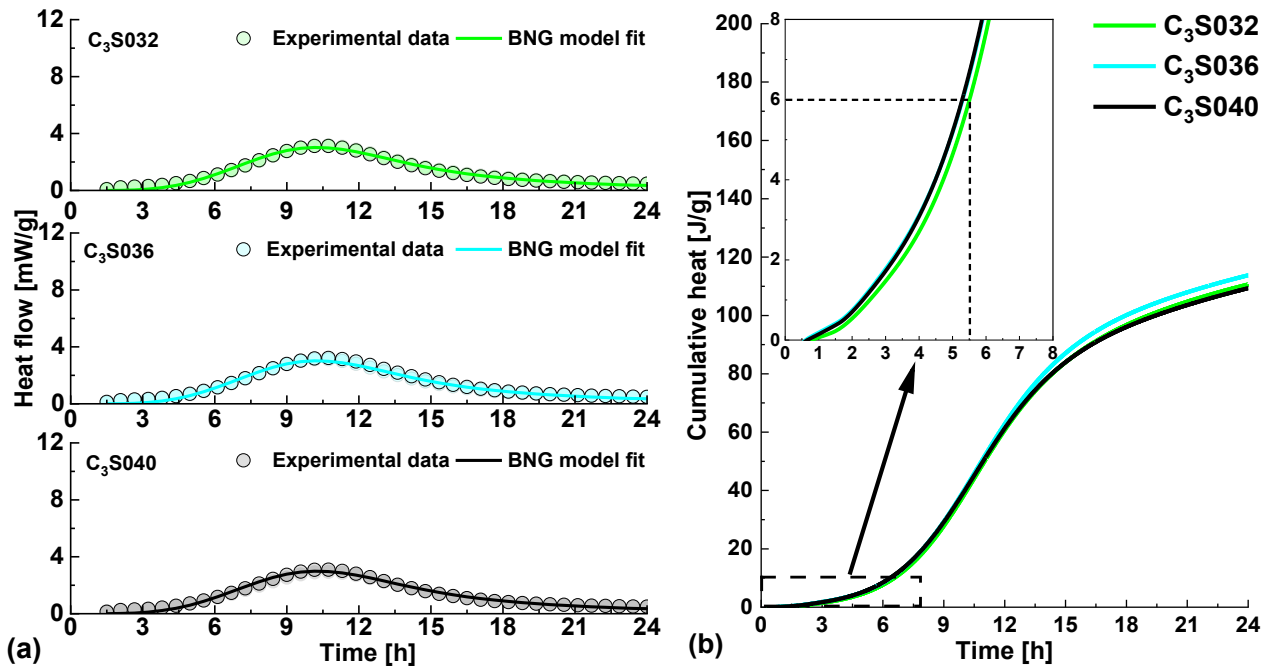


Fig. 6 Heat flow (a) and cumulative heat (b) of C_3S pastes with water-to-solid ratios from 0.32 to 0.40. The fitted BNG curves are shown together with the heat flow data.

Fig. 7 presents similar plots for pastes with a constant $w/s = 0.40$ and increasing calcium nitrate additions (0, 3, and 6 wt.% by C_3S weight). The heat flow curves show

that calcium nitrate significantly accelerates the hydration process, shifting the exothermic peak to earlier times and increasing the maximum heat flow, which is comparable to the effect found in cement pastes [67]. Again, the BNG model provides accurate fits to the experimental data, particularly during the acceleration and peak regions. The cumulative heat plots indicate that both the rate and extent of hydration increase with higher calcium nitrate dosage, confirming its effectiveness as a chemical accelerator. When comparing the time required to reach 6 J/g of cumulative heat, a clear trend emerges: with increasing calcium nitrate content, the time decreases from 5 h 10 min (0 wt.%) to 4 h 10 min (3 wt.%) and further to 2 h 53 min (6 wt.%), providing quantitative evidence of the accelerating effect.

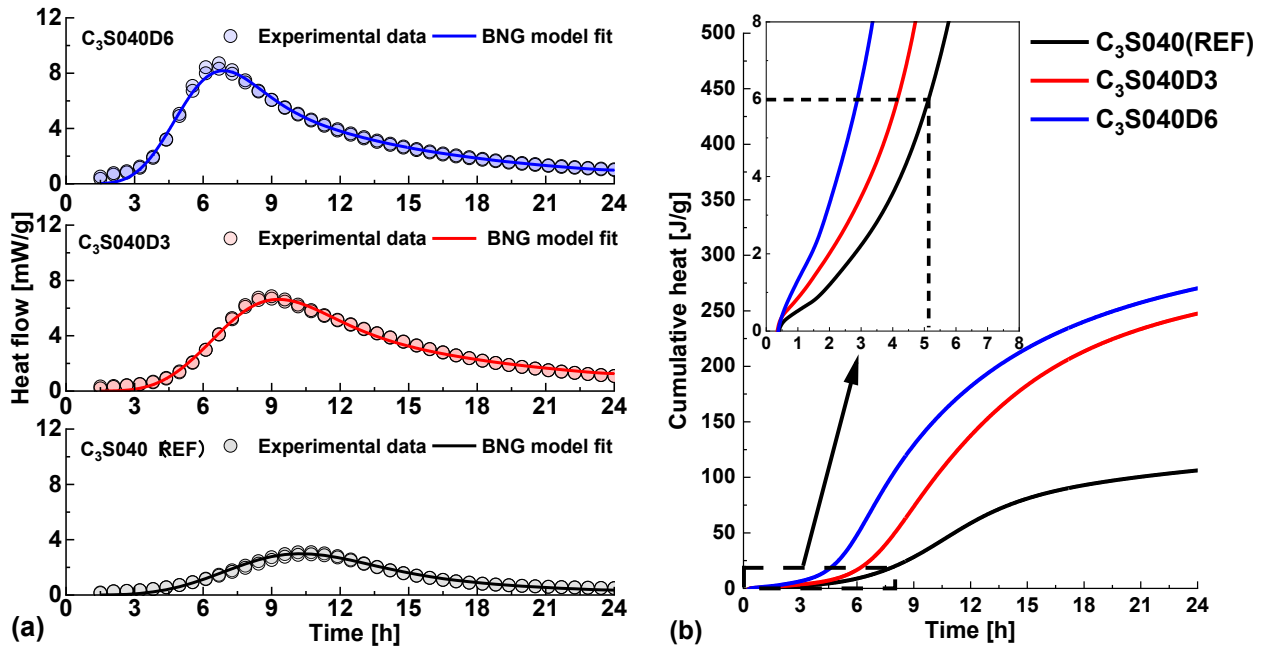


Fig. 7 Heat flow (a) and cumulative heat (b) of C₃S pastes with calcium nitrate dosages from 0 to 6.0 wt.% by mass of C₃S. The fitted BNG curves are shown together with the heat flow data.

Figs 6 and 7 demonstrate that the BNG model reliably captures hydration kinetics across various mixture designs. These results confirm that hydration behavior can be effectively modulated through both physical parameters (w/s) and chemical composition (admixtures), with the BNG model providing a unified framework for quantifying and comparing these effects. The fitted parameters, including G , I_B , t_0 , A and normalized root mean square error (NRMSE) and the coefficient of determination

(R^2), are summarized in Table 3. In addition, according to the BNG model, K_N and K_G represent independent hydration rates on the surface of cement particles and within the pore space, respectively, and are defined as follows:

$$K_N = (I_B O_b)^{1/4} G^{3/4} \quad (23)$$

$$K_G = O_b \cdot G \quad (24)$$

Table 3 Fitting results of the BNG model using heat flow data

	G [$\mu\text{m h}^{-1}$]	I_B [$\mu\text{m}^2 \text{h}^{-1}$]	t₀ [h]	A	NRMSE	R²
C₃S032	0.155	0.064	1.694	32.6	0.083	0.988
C₃S036	0.173	0.040	1.112	32.2	0.084	0.988
C₃S040(REF)	0.177	0.034	0.788	31.5	0.088	0.986
C₃S040D3	0.122	0.209	1.767	80.8	0.063	0.991
C₃S040D6	0.139	0.552	1.600	82.2	0.048	0.993

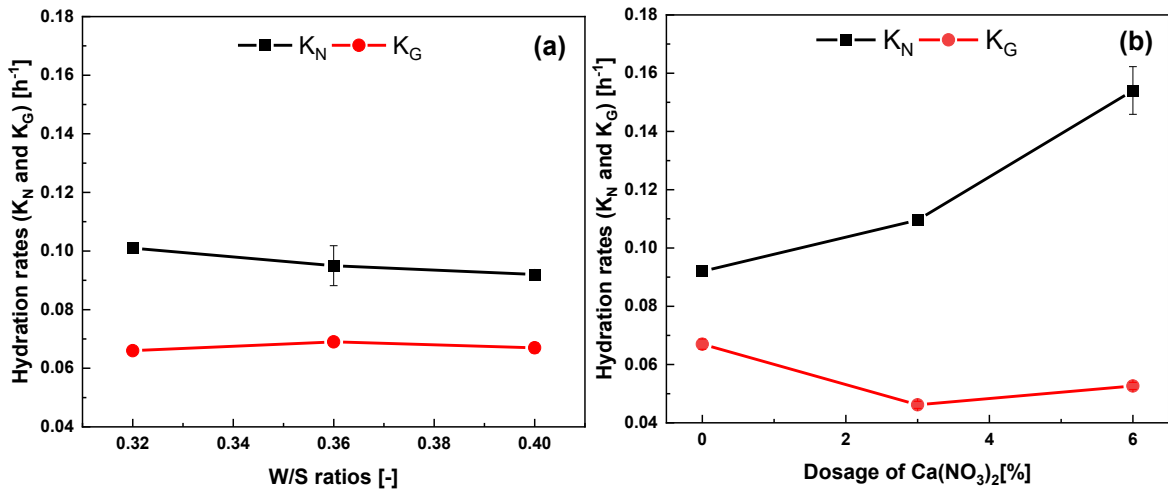


Fig. 8 The reaction rates on boundary (K_N) and in pore space (K_G) calculated from heat flow data with boundary nucleation growth (BNG) model

Fig. 8 illustrates the hydration rates on the boundary surface (K_N) and in the pore space (K_G), as derived from heat flow data using the Boundary Nucleation and Growth (BNG) model. In Fig. 8a, both K_N and K_G remain relatively stable across different water-to- C_3S ratios, with K_N showing a slight decline and K_G exhibiting a stable value after a w/s ratio of 0.36. In Fig. 8b, increasing the dosage of $\text{Ca}(\text{NO}_3)_2$ significantly enhances K_N , particularly at 6 wt.%, while K_G first decreases and then slightly rises, suggesting differential sensitivity of boundary and pore space reactions to chemical acceleration.

These trends are generally consistent with findings reported in the literature [68–70], supporting the validity of the fitted parameters.

4.2 The transverse relaxation time of C₃S paste

Fig. 9 shows the evolution of the main transverse relaxation time (T_2) over hydration time, reflecting changes in pore structure during early hydration. T_2 here refers to the weighted relaxation time of water in immature or capillary pores ($T_{2,P}$, typically 2-100 ms as shown in Fig. 3). Fig. 9a presents results for pastes with different water-to-C₃S ratios ($w/s = 0.32, 0.36, 0.40$), while Fig. 9b focuses on samples with a constant $w/s = 0.40$ and varying accelerator dosages (0, 3, and 6 wt. %). The corresponding changes in the total hydrogen proton signal intensity, which reflect water consumption and hydration progress, are provided in the **Supplementary Materials (Fig. S2)** as additional supporting information.

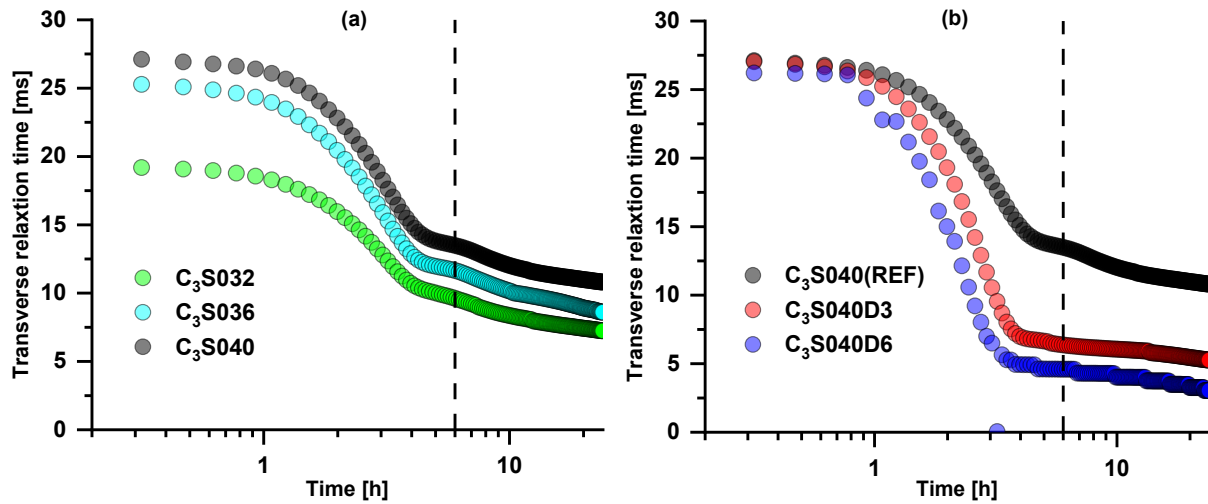


Fig. 9 T_2 value of the main peak as a function of time in C₃S pastes prepared with various water-to-C₃S ratios (a) and calcium nitrate dosages (b). A dashed line at 6 h is included for comparison.

In Fig. 9a, T_2 remains stable during the early stage and then drops gradually, indicating a transition from larger pores to smaller or more water-confined ones. While all samples follow a similar trend, higher w/s ratios tend to maintain larger T_2 values after the transition, reflecting a more open pore structure [51]. However, the timing of this transition is not significantly affected by the w/s ratios, suggesting that within this range, the increased water content does not substantially alter the early hydration

kinetics or the onset of pore structure densification (in agreement with calorimetry).

In Fig. 9b, both 3 wt.% and 6 wt.% additions of calcium nitrate result in an earlier and sharper decline in T_2 times compared to the reference, indicating accelerated hydration kinetics. This acceleration is likely attributed to calcium nitrate promoting faster dissolution of C_3S and facilitating the nucleation of hydration products. The 6 wt.% sample shows the most pronounced shift, further confirming the admixture's role in enhancing the microstructural development of the paste.

In both cases with $Ca(NO_3)_2$, the characteristic T_2 drop appears earlier than the transition point t_0 derived from fitting hydration heat data with the Boundary Nucleation and Growth (BNG) model. The low-field NMR detects the water signals among the solids, which begin to change earlier than hydration products begin forming on particle surfaces. This temporal offset has been observed in cement systems, as reported by She et al. [71]. In the study by Bligh et al. [72], this is particularly evident in the comparison between heat flow and the evolution of the relaxation time, namely $T_{2, \text{long}}$. Most importantly, C_3S offers a key advantage over cement samples for NMR-based pore structure analysis due to its very low content of paramagnetic components such as iron oxides or transition metal impurities (e.g., Fe^{3+} , Cu^{2+}). As a result, interference with ^1H NMR signals is minimized, enabling more reliable characterization of early-stage pore structures. This is particularly important because even trace amounts of paramagnetic ions can significantly shorten relaxation times and distort NMR measurements [73,74]. It is well established that NMR relaxation rates correlate with pore size or interparticle space. In the fast diffusion regime, T_2 is primarily governed by the surface-to-volume ratio (S/V) [75]:

$$\frac{1}{T_2} = \frac{1}{T_{2,\text{surf}}} = \rho_2 \frac{S}{V} = \rho_2 \frac{1}{R} \quad (25)$$

Here, ρ_2 is the surface relaxivity for T_2 , which characterizes relaxation at the pore surface. Since the bulk relaxation time of water at room temperature (around 3 s) is much longer, it can often be neglected for materials with sufficiently small pores [51,75]. Here, the initially measured T_2 relaxation time at 10 min after paste preparation and the interparticle distance calculated using Eq. 5 are plotted in Fig. 10.

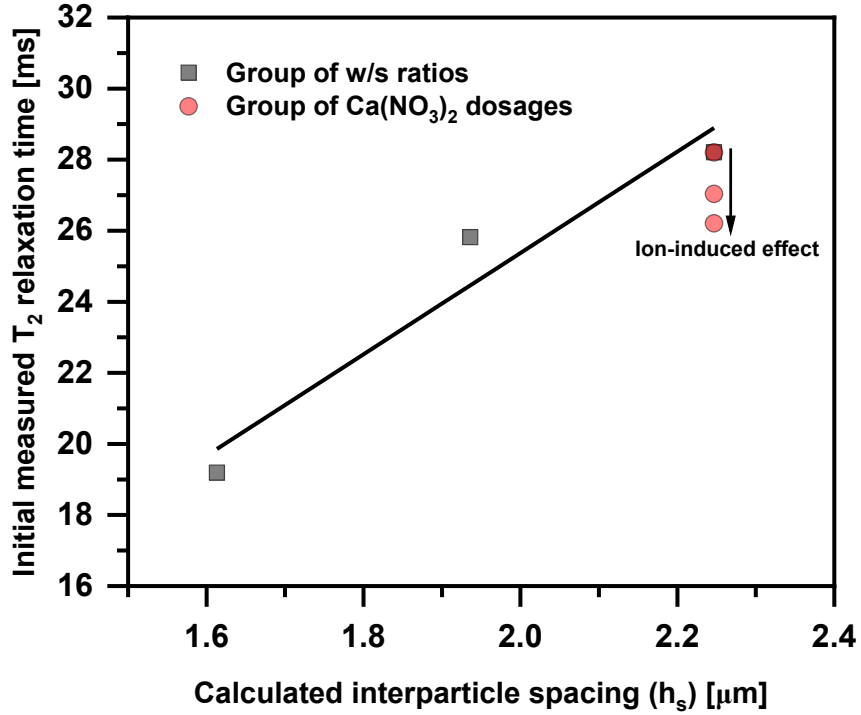


Fig. 10. Correlation between the initially measured T_2 relaxation time at 10 min after paste preparation and the calculated interparticle distance (H_s).

As expected, the initially measured T_2 relaxation time and the calculated interparticle distance exhibit a positive correlation across the samples with varying w/s ratios, suggesting that the two equations (Eq. 5 and Eq. 25) used to estimate the initial interparticle spacing are mutually consistent. Additionally, although the calculated spacing remains constant, the addition of calcium nitrate results in shorter T_2 values. This can be attributed primarily to the ion-induced effect of calcium and nitrate ions, which accelerate transverse relaxation, or possibly to the influence of early hydration product formation. In our model, the assumption of constant initial particle spacing (in the samples of w/s = 0.40 without and with $\text{Ca}(\text{NO}_3)_2$) is supported by the relatively stable T_2 values shown in Fig. 9, indicating that this aspect of the model is theoretically consistent.

4.3 Structural build-up and modeling

Fig. 11 shows the evolution of structural build-up over time for C_3S pastes with different water-to-solid ratios and calcium nitrate dosages. The structural response was characterized by two complementary quantities: the increase in apparent static yield stress obtained from slow penetration tests ($\Delta\tau_0$, Figs. 11a, 11b) and the relative

storage modulus obtained from SAOS time sweep tests ($\Delta G'$, Figs. 11c, 11d).

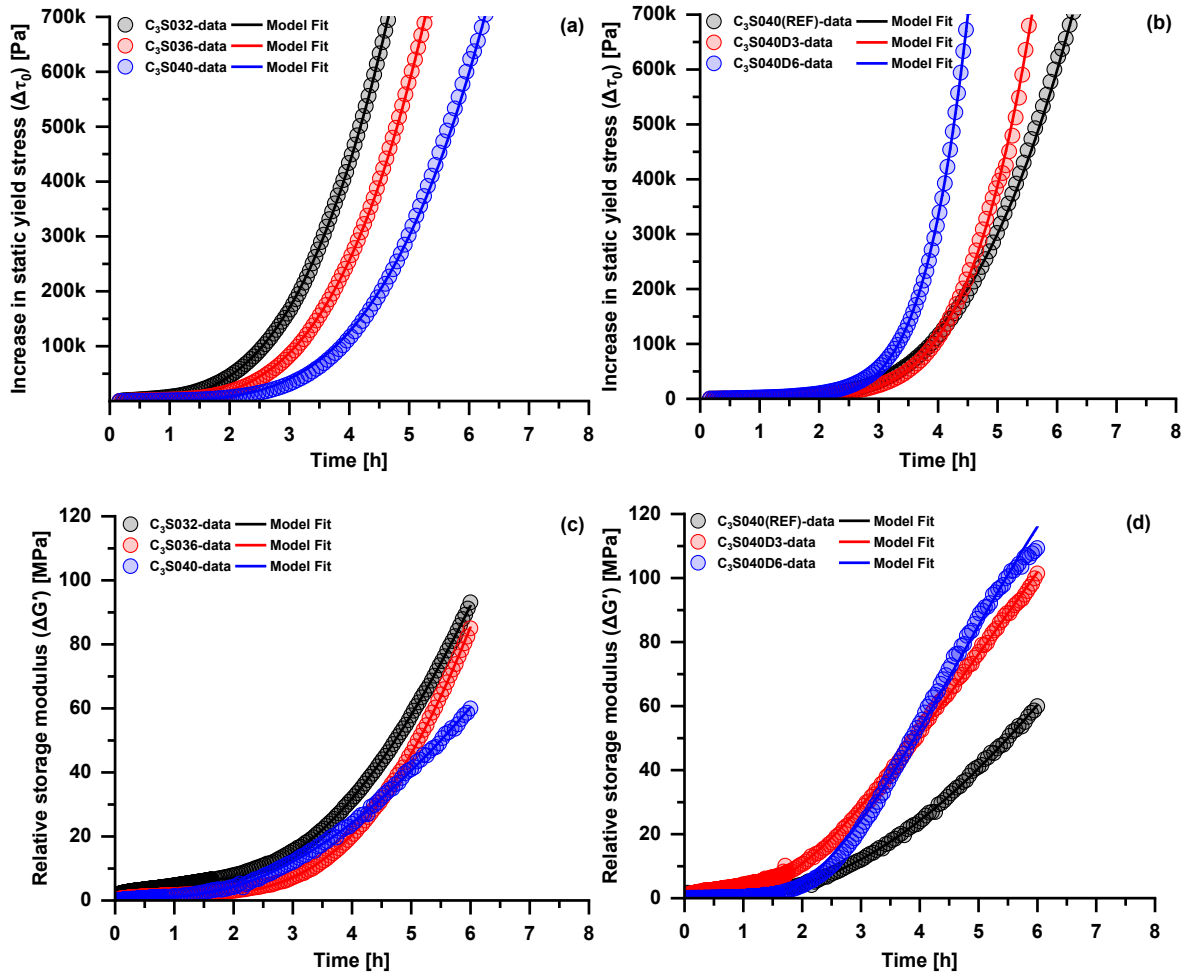


Fig. 11 Structural build-up of C₃S pastes characterized by the increase in apparent static yield stress $\Delta\tau_0$ from slow penetration tests (a, b) and the relative storage modulus $\Delta G'$ from SAOS time sweep tests (c, d). Symbols represent experimental data, and solid lines represent model fits.

Here, $\Delta\tau_0$ and $\Delta G'$ were calculated by subtracting the initial values from the measured responses, i.e., $\Delta\tau_0(t) = \tau_0(t) - \tau_0(0)$ and $\Delta G'(t) = G'(t) - G'(0)$. These quantities represent the time-dependent increase in penetration resistance or small-strain stiffness during structural build-up. The corresponding calculated structural responses obtained from Eq. 17 are also shown. In the penetration tests, all samples exhibit a slow initial increase in $\Delta\tau_0$, followed by a sharp acceleration after approx. 2–3 h. As expected, lower w/s ratios result in a steeper and earlier increase in $\Delta\tau_0$, indicating faster structural build-up due to lower water availability. The SAOS tests display some irregularities, particularly before 4.5 h, during which the sample with w/s = 0.36

unexpectedly shows a lower $\Delta G'$ than the $w/s = 0.40$ sample. Nevertheless, the overall evolution of $\Delta G'$ indicates progressive structural build-up and is broadly consistent with the trend observed in the slow penetration tests.

Fig. 11b focuses on C_3S pastes with a fixed w/s ratio of 0.40 and increasing calcium nitrate additions (0, 3, and 6 wt.%). The addition of calcium nitrate clearly accelerates the increase in apparent static yield stress $\Delta\tau_0$. The 6 wt.% dosage leads to the earliest and most rapid increase in $\Delta\tau_0$, highlighting its strong effect in promoting early structural build-up and network rigidity. However, for the 3 wt.% dosage sample ($C_3S040D3$), $\Delta\tau_0$ remains lower than that of the reference sample ($C_3S040(REF)$) during the first 4 h. This behavior is unexpected but consistent with earlier results for cement pastes [76], suggesting a more complex interaction at lower admixture dosage, possibly involving delayed percolation or competing effects between ionic acceleration and early structure destabilization. This point will be discussed in a later section together with other measurements. The SAOS results in Fig. 11d further support the effect of calcium nitrate addition, showing an increase in the final relative storage modulus $\Delta G'$ with higher dosages. However, prior to 3.5 h, the 6 wt.% sample exhibits a lower $\Delta G'$ than the 3 wt.% sample, suggesting that the early-age small-strain response may be non-monotonic.

Table 4 Fitted parameters of the proposed model for $\Delta\tau_0$ and $\Delta G'$

	Response type	α	β	R^2	ND
C₃S032	Penetration	2.42×10^7	1.64	0.9998	0.0171
	SAOS	7.43×10^2	1.00	0.9995	0.0193
C₃S036	Penetration	2.85×10^7	1.88	0.9997	0.0214
	SAOS	1.54×10^3	1.47	0.9998	0.0170
C₃S040(REF)	Penetration	2.10×10^7	2.00	0.9975	0.0639
	SAOS	5.97×10^2	1.00	0.9995	0.0203
C₃S040D3	Penetration	1.02×10^8	2.89	0.9983	0.0642
	SAOS	5.64×10^2	0.63	0.9989	0.0221

C₃S040D6	Penetration	1.71×10 ⁸	3.51	0.9992	0.0474
	SAOS	5.36×10 ²	0.77	0.9954	0.0496

To evaluate the proposed fractal-based model, the experimental structural responses were fitted separately using the slow penetration and SAOS data. As shown in Fig. 11, the model reproduces the main time-dependent trends of structural build-up under different water contents and calcium nitrate dosages. The fitted parameters and statistical indicators are summarized in Table 4. For the penetration tests, all datasets show correlation coefficients above 0.99 and normalized errors below 0.07, indicating good agreement between the model and the measured increase in apparent static yield stress, $\Delta\tau_0$.

The SAOS data were also fitted using the same framework, with $\Delta G'$ used as the structural response. The fitted trends are generally consistent with the experimental evolution of $\Delta G'$. It should be noted that the slow penetration test and SAOS time sweep probe different mechanical responses: the former reflects the increase in penetration-based apparent static yield stress, whereas the latter reflects the increase in small-strain stiffness. Therefore, the fitted parameters obtained from the two methods should not be treated as directly equivalent. In view of this distinction, the following analysis of the physical meaning of the fitted parameters focuses only on those derived from the penetration tests. This is because $\Delta\tau_0$ from penetration tests has a more direct interpretation in the context of structural build-up under static conditions. The SAOS-derived parameters, while statistically reliable, reflect the evolution of small-strain oscillatory stiffness, which is frequency-dependent and less directly linked to the network formation and hydration processes of interest. Therefore, the penetration results are used as the primary basis for parameter interpretation, and the SAOS results are retained as qualitative complementary evidence.

4.4 Analysis of fitted parameters

4.4.1 Morphology of hydrates and their relationship to fractal-based β

Next, we discuss the scientific implications of the parameters obtained from the model fitting. These parameters not only enable an accurate representation of structural build-up, characterized by penetration resistance but also provide insights

into the underlying mechanisms governing the evolving connectivity within the hydrate structure. Fig. 12a presents the relationship between the fitted β parameter and the apparent size of hydrate-related nanoparticles obtained from DLS in C_3S pastes with varying water-to-solid (w/s) ratios, while Fig. 12b shows the same relationship under different calcium nitrate dosages. These DLS results are interpreted as supportive evidence for morphological trends, together with SEM observations and the systematic evolution of the fitted β parameter, rather than as an exact determination of absolute hydrate size. SEM images of samples C_3S032 , C_3S040 , and $C_3S040D3$ after 4 h of hydration are shown in Fig. 12c.

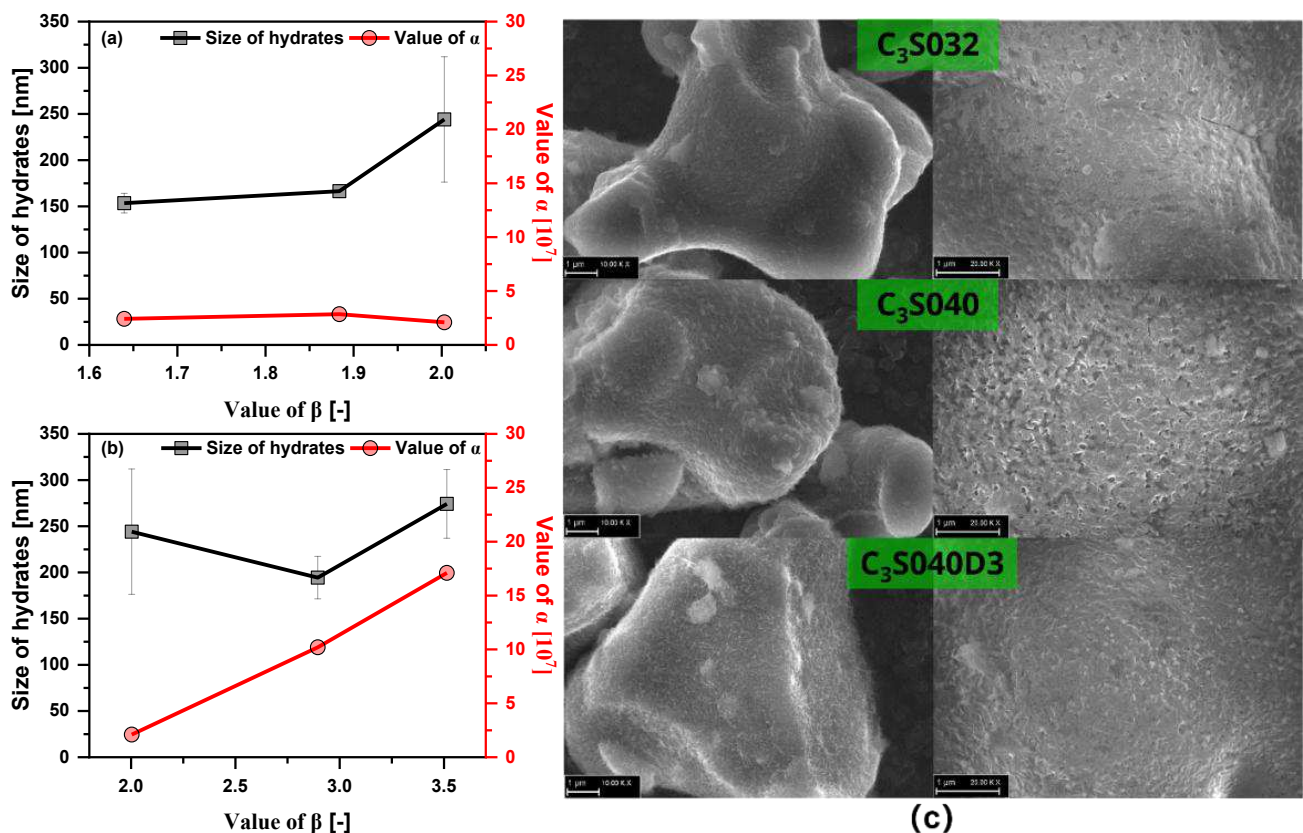


Fig. 12 Relationships between fitted β , apparent hydrate-related nanoparticle size obtained from DLS, and fitted α for (a) w/s ratios and (b) $Ca(NO_3)_2$ dosages, with (c) SEM images of C_3S032 , C_3S040 , and $C_3S040D3$ at 4 h hydration.

A general trend is observed: higher β values are associated with larger apparent hydrate-related nanoparticle sizes. This suggests that β , a growth-related parameter in the constitutive model, captures aspects of morphological growth and the spatial development of hydration products. In Fig. 12a, increasing the w/s ratio from 0.32 to 0.40 leads to progressively higher β values and a corresponding increase in hydrate

size, while α remains relatively unchanged. This behavior is consistent with greater spacing and water availability at higher w/s ratios, which allows hydration products to grow with fewer spatial constraints, resulting in coarser and less compact structures of hydrates. Our Monte Carlo simulations (Fig. 5) support this interpretation. Shorter line segments (250-unit length) with the same number of points and sticking probability generate more extended fractal "tree" structures, resembling loosely packed hydrates. This implies that reduced surface area and lower spatial constraints in high w/s systems promote larger but less dense hydration morphologies. These model-derived insights are also well supported by the SEM images of C₃S032, C₃S040, and C₃S040D3. For instance, C₃S040, which has a higher β value than C₃S032, exhibits visibly larger and more loosely packed hydrates, reflecting a more open microstructure. In contrast, C₃S032 shows smaller and more densely clustered hydrates, consistent with a lower β value and more restricted growth.

However, as shown in Fig. 12b, the β value exhibits a non-linear response to increasing calcium nitrate dosage, indicating a more complex interplay between nucleation kinetics and hydrate growth. Interestingly, a strong linear correlation is observed between β and α (Fig. 12b), as defined in Eq. (26) [35]:

$$\alpha = a_1 b_1 u_1 S \left| f_b - f_{ves} \right| f(c) (V_0 u_2 u_3)^{\frac{\beta}{2}} \quad (26)$$

where the two parameters are linked through constants V_0 , $f(c)$, b_1 , u_1 , u_2 and u_3 , and S is the effective contact area of the hydrates. Assuming that interparticle forces remain approximately constant across different conditions, α can be interpreted as being primarily governed by the number of solid–solid bridges or nucleation events, denoted as a_1 , which is correlated with β .

Among all samples, C₃S040D3 (with 3.0 wt.% calcium nitrate) shows the smallest apparent hydrate-related clusters, as indicated by SEM and DLS. This observation is consistent with the dissolution–precipitation theory: increased Ca²⁺ concentration enhances supersaturation, accelerates nucleation, and leads to the formation of numerous growth fronts. As a result, the available solutes are partitioned among more nuclei, limiting individual growth and resulting in smaller particle sizes [77]. According

to commonly used formulations derived from classical nucleation theory [77,78], the nucleation rate J increases rapidly with supersaturation and can be expressed as:

$$J = C \exp\left(-\frac{B}{(\ln S)^2}\right) \quad (28)$$

$$L = \left(\frac{1}{J}\right)^{1/3} \quad (29)$$

where J is the nucleation rate, S is supersaturation, and B depends on interfacial energy and molar volume, and C is a constant. Equation (28) has been widely applied in the analysis of crystallization-driven microstructure refinement. This relation illustrates that the average crystal size L scales inversely with the cube root of the nucleation rate J . As supersaturation increases and nucleation is enhanced, the solute is partitioned among more nuclei, reducing the size of individual crystals. Therefore, despite the β value being relatively high in C₃S040D3, the simultaneously high α value indicates a larger number of hydration products.

This combination suggests that a large number of small hydration products were formed, driven by enhanced nucleation. In this context, α reflects the number of bridges or nucleation events, while β characterizes the spatial arrangement of the hydration products. The observed microstructural refinement is therefore best explained by the dominant influence of α , in line with the dissolution-precipitation mechanism. These results suggest that the proposed model not only captures macroscopic rheological behavior but also provides useful insight into early-age microstructural evolution. The consistency between the model parameters, SEM observations, DLS measurements, and classical nucleation theory supports the proposed interpretation. Together, these multiscale lines of evidence suggest that the parameters α and β can help link microscale mechanisms to macroscale rheological behavior during C₃S hydration.

4.4.2 Filling properties of hydration products

The relationship between the fitted β values and the change in T_2 relaxation time (ΔT_2), which reflects the extent of pore filling and water confinement by hydration products, is shown in Fig. 13. To ensure a fair comparison, the ΔT_2 values, defined as $\Delta T_2 = T_2(t) - T_2(0)$, were determined at the point when approx. 6 J/g of hydration heat

had been released from the C_3S paste. The threshold of 6 J/g was adopted to ensure temporal comparability between calorimetric and penetration data: lower values would place some samples (e.g., $C_3S040(REF)$) within the induction period, whereas higher values would shift the corresponding time point beyond the penetration testing window for other samples (e.g., $C_3S040D6$).

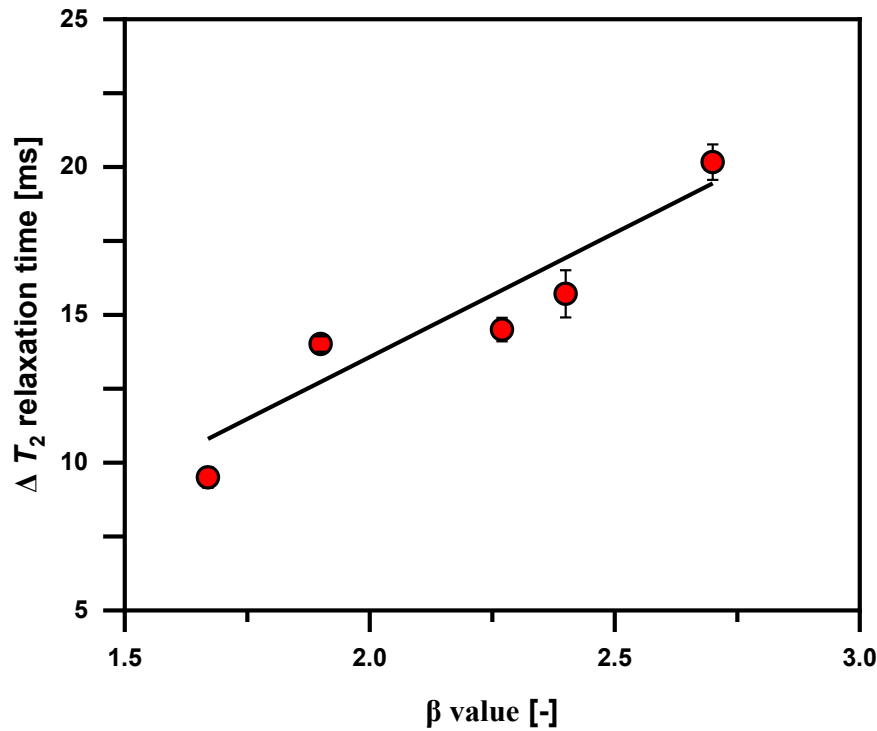


Fig. 13 Relationship between the fitted β values and the T_2 relaxation time difference (ΔT_2) at a comparable hydration degree of 6 J/g

Fig. 13 reveals a clear positive correlation, indicating that larger β values are associated with greater ΔT_2 . As discussed in the previous section, higher β values correspond to lower fractal dimensions, which describe simpler morphologies of the hydration product. For instance, hydrates with high β values tend to form more open, “cotton-like” C–S–H networks. Such morphologies influence the pore structure by filling the available space more effectively, leading to smaller pore sizes at a comparable hydration extent. This distinction highlights that β reflects not only the morphology of C–S–H itself but also the resulting pore structure. Accordingly, β provides a direct link between the evolution of rheological properties during structural build-up and the pore-scale changes captured by NMR, offering a coherent framework for understanding how mechanical development is connected to hydration-driven microstructural evolution.

4.4.3 Time-dependent β and its implications

The time-dependent evolution of the fitted β values is shown in Fig. 14 for C_3S pastes, together with two reference OPC pastes at water-to-cement ratios of 0.36 and 0.40 from Ref. [35]. Unlike the previous sections, where β was fitted over the whole selected structural build-up window, here β is evaluated over successive time intervals to track the evolution of hydrate morphology during early hydration.

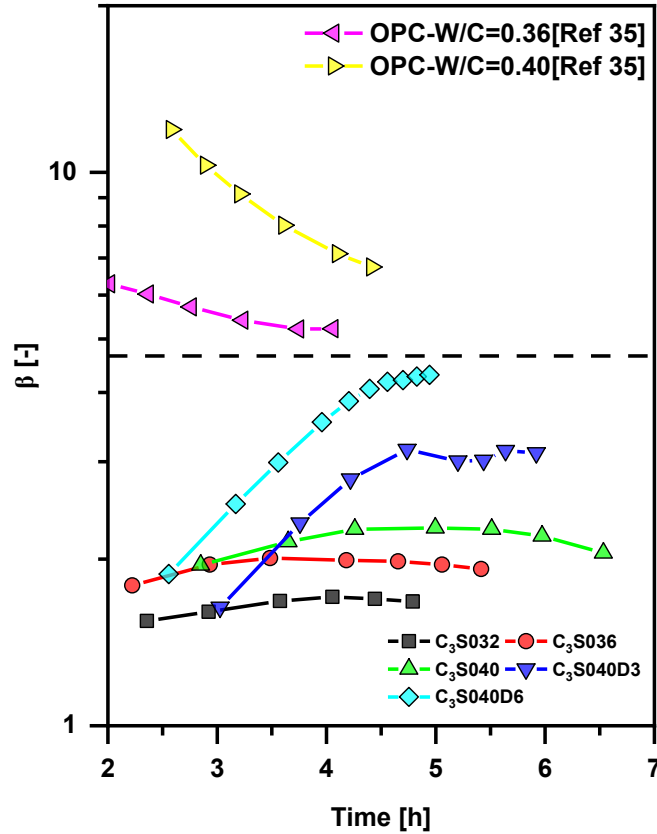


Fig. 14 Time-dependent evolution of fitted β values for C_3S and OPC pastes. For C_3S pastes, β values were fitted at selected penetration-force levels of 5, 15, 30, 60, 90, 120, 150, and 180 N. For OPC pastes, β values were taken from Ref. [35] at yield stress levels of 500, 1000, 2000, 4000, 8000, and 12000 Pa.

As defined in this study, a higher β corresponds to a lower fractal dimension, indicating more open and loosely packed hydrate morphologies. In contrast, a lower β indicates a more compact and internally connected hydrate structure. This interpretation is consistent with the Monte Carlo results in Fig. 5d, where lower fractal dimensions are associated with more open cluster structures.

Among the C_3S pastes, C3S040D6 shows the most pronounced increase in β with time, while C3S040D3 exhibits a similar but weaker trend. This indicates that calcium

nitrate promotes the formation of increasingly open hydrate structures during the investigated period. The increase in β can be explained by the Monte Carlo simulations, where randomly walking particles initially form relatively compact clusters near the boundary. As the number of attached particles increases, growth tends to occur preferentially on the outer branches, limiting inward diffusion and leading to a more open, tree-like morphology. Therefore, the increase in β captures this structural simplification process, reflecting the evolution of internal connectivity within hydration products from an initially compact and complex configuration toward a more open, branched morphology.

For C_3S pastes without accelerators, especially C3S040, β shows a slight decrease after approximately 5 h. A similar decreasing trend is also observed in the OPC reference pastes from Ref. [35] shown in Fig. 14. This increase in structural complexity may be associated with changes in particle aggregation behavior, as indicated in Fig. 5 and further visualized in the **supplementary video**. From a hydration chemistry perspective, pure C_3S hydration mainly produces C–S–H and portlandite [79–81]. The early C–S–H is generally low-crystalline and loosely packed, while continued hydration may promote increased connectivity and local ordering of C–S–H [65]. Therefore, the slight decrease in β at later times may reflect the transition from initially open hydrate clusters toward more connected and compact hydrate networks. Overall, the time-dependent β analysis suggests that hydrate morphology does not evolve monotonically but may undergo structural simplification followed by partial re-complexification during early hydration. These results suggest that the proposed model provides a useful bridge between hydrate-scale topology and macroscopic structural build-up during the early-age period.

4.5 Model limitations and applicability

The proposed framework provides a physically informed way to relate hydration kinetics, hydrate-scale morphology, and early-age structural build-up. Nevertheless, several simplifications should be considered when interpreting the model parameters.

The BNG model is used to estimate the transformed volume fraction of hydration products, $X_T(t)$, which serves as input for the hydrate-bridging model. Therefore, the

framework is mainly applicable within the early-age window where hydration evolution and mechanical response can still be meaningfully related. Very rapid reactions, such as those associated with C_3A hydration, may not be fully captured. Thus, the present model is most directly applicable to C_3S -based systems, while extension to multiphase cement systems requires additional treatment of overlapping reactions and phase-specific contributions.

Although the fitted parameters α and β have physical meanings, they are still obtained through model fitting and should not be treated as direct material constants. Their values may be affected by the experimental method used to characterize structural build-up. In particular, β is a time-window-dependent descriptor: values fitted over different hydration intervals may differ because hydrate morphology evolves continuously. Therefore, β is used here to describe the relative evolution of internal connectivity within a defined time window, rather than to represent an absolute fractal dimension.

Beyond parameter interpretation, a further simplification lies in the model structure itself. The current model assumes that all hydration products contribute equally to bridge formation, whereas in reality, the mechanical effectiveness of a hydrate bridge likely depends on its local position (e.g., at interparticle contacts versus in pores) and its intrinsic stiffness, which may vary with hydration time and local chemistry.

The Monte Carlo simulations also involve simplifications. The simulated particles are idealized geometrical units, and their aggregation is governed by simplified random-walk and sticking rules. In addition, the simulations are performed in two dimensions, whereas real hydrate aggregation and pore filling occur in three-dimensional space. Although the 2D simulations with circular, triangular, and square particles support the robustness of the scaling relationship, real C–S–H or early hydration products may involve more complex anisotropic growth, chemical heterogeneity, and time-dependent reorganization that are not explicitly resolved here.

5 Conclusions and outlooks

Understanding early-age microstructural development is essential for interpreting structural build-up in reactive cementitious suspensions. In this study, a modelling

framework integrating BNG kinetics with a fractal-based hydrate-bridging model was developed to link hydration heat release, hydrate-scale morphology evolution, and macroscopic structural build-up in C_3S suspensions.

The proposed framework captures the evolution of structural build-up across different water-to-solid ratios and calcium nitrate dosages. A key model-derived parameter, β , serves as a structural descriptor of evolving hydrate morphology and internal connectivity within hydration products. The trends in β are consistent with hydrate-related nanoparticle sizes measured by dynamic light scattering (DLS) and with microstructural features observed by scanning electron microscopy (SEM). In calcium nitrate-modified systems, the reduced hydrate size agrees with classical nucleation theory, where enhanced ionic strength promotes nucleation and restricts individual crystal growth, leading to finer microstructural features.

At comparable hydration levels, β shows a positive correlation with the T_2 relaxation time difference obtained from ^1H NMR, suggesting that hydrate morphology affects pore filling and water confinement. The temporal evolution of β further indicates an initial phase of structural simplification followed by partial re-complexification, implying dynamic morphological transitions of hydration products during early hydration. This evolution is consistent with Monte Carlo simulations and supports the interpretation of β as a model-derived descriptor of internal connectivity.

These findings show that early-age structural build-up in C_3S suspensions is governed not only by the amount of hydration products, but also by their spatial arrangement, morphology, and internal connectivity. The proposed framework provides a microstructure-informed route for linking hydrate-scale topology with macroscopic rheological evolution. The proposed framework may provide a broader basis for understanding structure formation and rheological evolution in other reactive particulate systems governed by interfacial growth and disordered aggregation.

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