

Physicochemical characteristics and valorization of hydrogen-based mineral phase transformation iron ore tailings for cementitious applications

Yanfeng Fang¹, Junying Zan¹, Xiao Li¹, Changwei Xu¹, Xiaolei Wang², Weidong Yan²

¹ School of Material Science and Engineering, Shenyang Jianzhu University, Shenyang 110168, China

² School of Civil Engineering, Shenyang Jianzhu University, Shenyang 110168, China

Corresponding author: 13191739958@163.com (Weidong Yan)

Abstract: The rapid development of hydrogen-based mineral transformation technologies has generated increasing amounts of iron ore tailings with distinct physicochemical characteristics, creating new challenges for resource utilization. This study investigates the mineralogical characteristics and cementitious utilization potential of hydrogen-based mineral phase transformation iron ore tailings (HMPT-IOTs). The effects of HMPT-IOTs incorporation on the hydration behavior, mechanical performance, and microstructural evolution of cement-based materials were systematically evaluated. The results indicate that HMPT-IOTs mainly consist of Fe-containing phases and silicate minerals, and their heterogeneous particle characteristics provide potential reactive sites in cementitious systems. The incorporation of HMPT-IOTs influences hydration kinetics by modifying early-age reaction processes. Among the investigated mixtures, the replacement of cement with 10 wt% HMPT-IOTs exhibited the most favorable performance, achieving a balanced improvement in mechanical properties and tailings utilization efficiency. Microstructural analysis revealed that HMPT-IOTs participate in hydration reactions and promote the formation of additional hydration products, contributing to matrix densification. This study demonstrates a feasible pathway for the high-value utilization of hydrogen-based iron ore tailings and provides insights into the physicochemical mechanisms governing their application in sustainable cementitious materials.

Keywords: hydrogen-based mineral phase transformation, iron ore tailings, mineral processing waste, resource utilization, cementitious materials

1. Introduction

Hydrogen-based mineral phase transformation (HMPT) technology has emerged as a promising clean metallurgical strategy for iron ore processing. By replacing coal with hydrogen as the reducing agent, it enables targeted phase conversion of iron ore into a magnetic form, achieving low-carbon and highly efficient resource utilization (Zhang et al., 2025). The core reaction involves the selective reduction of hematite (Fe_2O_3) to magnetite (Fe_3O_4) at moderate temperatures ($\sim 550^\circ\text{C}$): $3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$, avoiding over-reduction to metallic iron. Since 2025, the commissioning of million-ton-scale HMPT demonstration plants in Europe and China has marked a pivotal transition from laboratory development to industrial implementation (Wang et al., 2025; Ning et al., 2025). However, this industrial shift has led to the dramatic generation of hydrogen-based mineral phase transformation iron ore tailings (HMPT-IOTs) (Ning et al., 2025; Zhao et al., 2025). Compared with traditional coal-based reduction tailings—which typically contain high residual carbon, sulfur impurities, and inert silicates—HMPT-IOTs show distinctive mineralogical and morphological features: remarkably low unburned carbon ($<1\text{ wt}\%$), minimal sulfur, metastable Fe_3O_4 (30–45 wt%), and a rough particle surface (Ning et al., 2024). While conventional iron ore tailings (IOTs) have long been stockpiled in the open air in China—causing severe environmental issues such as land occupation and dust pollution (Moafak et al., 2022)—the emergence of HMPT-IOTs presents a new challenge and opportunity. The high-value utilization of these massive solid wastes is of great significance for ecological safety and resource

recovery (Russo et al., 2022; Wu et al., 2024). Notably, the transition to hydrogen-based reduction fundamentally modifies the mineral structure of the residues, converting them from inert silicates into reactive phases (e.g., metastable Fe_3O_4 and active SiO_2). This positions HMPT-IOTs not just as waste to be disposed of, but as a potential precursor for low-carbon cementitious materials.

Extensive research has been conducted globally to explore the comprehensive utilization of conventional IOTs across various sectors (Zhang and Li, 2018; Duan et al., 2016; Tang et al., 2022; Yang et al., 2020; Gu et al., 2023). Fundamentally, IOTs contain valuable components (Fe, Si, Al, Ca, Mg) (Kinnunen and Kaksonen, 2019; Han et al., 2022; Yang et al., 2024), enabling their application in chemical and agricultural industries (Sui et al., 2024). A primary focus, however, has been on their conversion into construction materials, particularly as supplementary cementitious materials (SCMs) (Gursel et al., 2014; Gou et al., 2019; Scrivener et al., 2018), to reduce reliance on traditional cement and promote sustainability (Gursel et al., 2014; Zhang et al., 2022; Kuranchie et al., 2015; Amjad et al., 2025). Although the favorable chemical composition (rich in Si, Al) and fine particle morphology of some IOTs make them theoretically suitable (Chen and Tang, 2025; Li et al., 2023; Chao et al., 2024; Wang et al., 2014; Liu et al., 2023), their practical application is hindered by intrinsic chemical inertia. To overcome this, activation treatments—primarily mechanical grinding—are essential to increase specific surface area and disrupt crystalline structures (Fang et al., 2025). For instance, Yao et al (Yao et al., 2020). demonstrated that mechanical activation enabled a 10–30% cement replacement while maintaining strength. The mechanical performance of iron tailings concrete under challenging environments (e.g., dry-wet cycles and negative temperature) has also been investigated (Liu et al., 2023). Furthermore, Tang et al (2022). highlighted that hydrogen reduction significantly enhances reactivity, underscoring the potential of phase transformation. However, these studies predominantly focus on modifying conventional IOTs, leaving the behavior of tailings generated directly from industrial HMPT processes largely unexplored.

Distinct from conventional residues, HMPT technology produces a novel type of tailings (HMPT-IOTs) with fundamentally altered mineralogy (Tian et al., 2025; Meng et al., 2025; Tang et al., 2024). These tailings exhibit remarkably low unburned carbon (<1 wt%) and sulfur impurities, while metastable Fe_3O_4 accounts for 30–45 wt% (Ning et al., 2024). Additionally, crystalline SiO_2 content is significantly higher, and particles are finer with a narrower size distribution (Ning et al., 2025). These unique characteristics—specifically the rough particle surface, irregular shape, and presence of metastable iron phases—suggest that HMPT-IOTs may possess both pozzolanic activity and nucleation effects superior to conventional IOTs. Consequently, HMPT-IOTs are a promising precursor for low-carbon cementitious materials. However, despite this potential, large-scale utilization faces challenges, including inconsistent pozzolanic reactivity (Yao et al., 2019), increased water demand (Li et al., 2022), and perturbed hydration kinetics from residual trace metals (Wang et al., 2023). Therefore, a comprehensive understanding of the specific hydration behavior and mechanism of HMPT-IOTs in cementitious systems is imperative.

Based on this, this study systematically investigates the hydration behavior of HMPT-IOTs in cement-based systems. Specifically, pozzolanic activity experiments combined with indicators such as chemically bound water, setting time, and chemical shrinkage, its influence on the cement hydration process was analyzed. Concurrently, isothermal calorimetry, SEM and TG/DTG were tested to reveal its microstructural evolution and hydration product characteristics.

2. Materials and experiments

2.1. Raw materials

HMPT-IOTs were obtained from the semi-industrial test, where the calcination temperature was 550 °C, with 10.0 m³/h of N₂, 1.5 m³/h of CO, and 4.5 m³/h of H₂ used, and the calcination time was 30 minutes. P·II 52.5 Portland cement, sourced from Qingdao Shanshui Cement Group Co., Ltd, was used in this study. And the key physical properties of the cement are summarized in Table 1 confirming its compliance with the national standard. Table 2 lists the chemical composition of cement and HMPT-IOTs, determined by X-ray fluorescence (XRF). The main chemical components of HMPT-IOTs are SiO_2 and Fe_2O_3 , and it belongs to the category of high-silicon iron tailings. The X-ray diffraction (XRD) pattern in 0 indicated that the main mineral phases of HMPT-IOTs are SiO_2 and Fe_3O_4 . The microscopic

morphology of HMPT-IOTs, presented in 0 showed that its surface is rough and the particle shape is irregular. The particle size distributions of HMPT-IOTs and cement determined by Malvern Mastersizer 2000 are shown in 0 The results reveal that the median particle size (d_{50}) of HMPT-IOTs is 16.2 μm , which is slightly larger than that of cement (12.5 μm). Similarly, the d_{90} value for HMPT-IOTs (53.3 μm) is also higher than that of cement (46.9 μm).

The ISO standard sand used in this experiment was provided by Xiamen Aisiou Standard Sand Co., Ltd.

Table 1. Physical-mechanical properties of cement

Cement	Specific surface area (m ² /kg)	Setting time (min)		Compressive strength (MPa)		Flexural strength (MPa)	
		Initial	Final	3 days	28 days	3 days	28 days
P·II 52.5	357	171	221	34.1	58.9	6.5	8.8

Table 2. Chemical composition of cement and HMPT-IOTs

Chemical Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Others
HMPT-IOTs	74.91	5.28	14.94	2.6	0.19	0.40	0.39	-	1.29
Cement	24.32	4.95	3.44	3.21	59.65	0.25	0.35	0.14	3.69

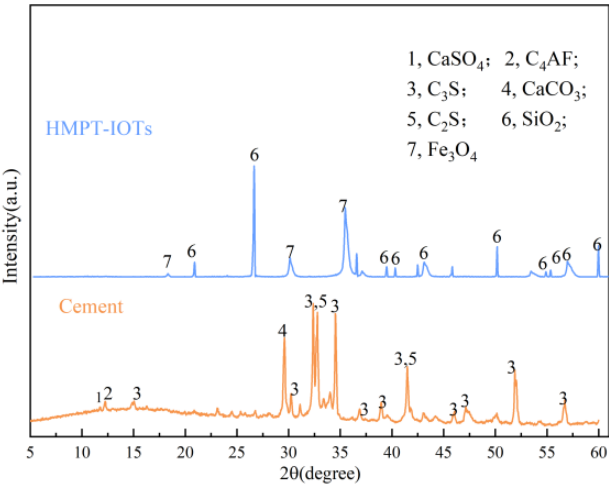


Fig. 1. XRD patterns of cement and HMPT-IOTs

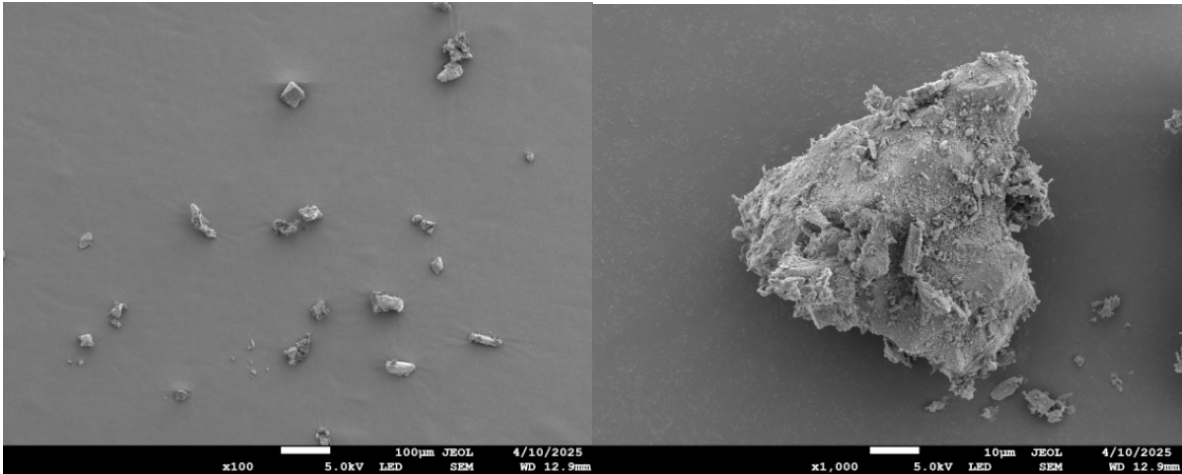


Fig. 2. SEM morphology of HMPT-IOTs

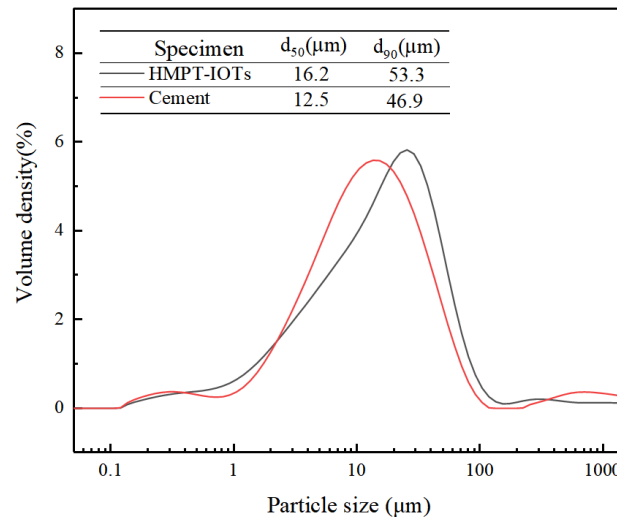


Fig. 3. Particle size distributions of cement and HMPT-IOTs

2.2. Sample preparation and experiments methods

2.2.1. Pozzolanic reactivity of HMPT-IOTs

The pozzolanic activity of HMPT-IOTs was determined using a modified lime adsorption method (Fang et al., 2024). A mixture of 30 wt% lime ($\text{Ca}(\text{OH})_2$) and 70 wt% HMPT-IOTs, with a w/c ratio of 0.3, was homogeneously prepared and cured in a standard environment ($20 \pm 1^\circ\text{C}$, relative humidity $\geq 95\%$) until 3 and 28 d respectively. The hydrated samples were dried at 60°C for 24 hours to minimize the adverse effects of evaporative water then TGA analysis was performed to evaluate the consumption of $\text{Ca}(\text{OH})_2$.

2.2.2. Preparation of cement pastes and mortars

HMPT-IOTs were utilized as SCMs to replace 10wt.%, 20wt.% and 30 wt.% of P·II 52.5 Portland cement in the preparation of paste and mortar samples. The preparation of paste adhered to the protocols in the Chinese standard “test methods for water requirement of normal consistency, setting time and soundness of Portland cements, GB/T 1346-2024”. The water requirement of normal consistency is 0.29 and the setting time of pastes containing HMPT-IOTs were tested according to the above-mentioned standard. The preparation of mortars adhered to the protocols in the Chinese standard “Test method of cement mortar strength (ISO method), GB/T17671-2021”. A water-to-cement (w/c) ratio of 0.43 and a cement-to-sand ratio of 1:3 was employed. After 24 hours of casting, the specimens were demolded and subsequently cured in a moist room, maintaining a relative humidity of 98% and a temperature of 20°C until the testing ages of 3 and 28 d. The flexural and compressive strengths of the mortar specimens were tested following GB/T 17671-2021. Three valid specimens were tested using a YAW-300 compressive and flexural integrated machine with a loading rate of 1.2 MPa/s, and the average value was calculated and recorded.

The overall hydration degree was quantified by determining the chemically bound water content of hardened pastes via the muffle furnace ignition method, conducted in accordance with GB/T 176-2017. Chemical shrinkage was assessed based on the absolute volume method in accordance with ASTM C1608 (Bouasker et al., 2008). To mitigate paste adhesion to the container wall, an improved rubber membrane encapsulation technique developed by Zhang et al. (Zhang et al., 2013) was adopted.

2.3. Characterization methods of hydrated paste

The paste specimens cured to the target age were first crushed and then immersed in isopropanol for at least 24 hours to displace and remove pore water, thereby effectively inhibiting further hydration. Thereby, the samples were placed in a vacuum drying oven at 50°C for 24 hours. Finally, the dried samples were ground and passed through a 200-mesh sieve (approximately $75\ \mu\text{m}$ aperture) for subsequent microstructural analysis. SEM observations were conducted on sputter-coated sample cross-sections using a Thermo Fisher Apreo 2C field-emission scanning electron microscope. TGA was

performed with a Mettler Toledo TG/DSC1 instrument, where samples were heated from room temperature to 900 °C at a rate of 10 °C/min under a nitrogen atmosphere. The composition and decomposition behavior of hydration products were identified by analyzing the characteristic mass-loss steps in the thermogravimetric curves. X-ray diffraction (XRD) was performed on powdered hydrated paste samples using a Bruker D8 Advance diffractometer with Cu K α radiation (40 kV, 40 mA) over a 2 θ range of 5–80° at a step size of 0.02°. X-ray fluorescence (XRF) was used to determine the chemical composition of raw materials (cement and HMPT-IOTs), as listed in Table 2. Isothermal calorimetry was conducted using a TAM-AIR calorimeter at 20 ± 0.1 °C. Cement pastes with a water-to-cement ratio of 0.5 were manually mixed for 2 min and then immediately loaded into glass ampoules. The heat flow and cumulative heat release were continuously recorded for 72 h.

All measurements were carried out in triplicate to ensure data reliability. For TG-DTG and XRD, representative curves are shown after confirming high reproducibility (relative deviation < 3%). The results are presented as mean ± standard deviation (SD). Error bars in the figures correspond to the SD calculated from three independent experiments. Specifically, for compressive and flexural strength, three valid specimens per group were tested, and the average with SD is reported.

3. Results and discussions

3.1. Pozzolanic reactivity of HMPT-IOTs

The TG/ DTG curves of HMPT-IOTs / lime pastes hydration for 3 d and 28 d are presented in Fig. 4. The theoretical decomposition weight loss of initial HMPT-IOTs/lime pastes in the range of 400 ~ 500 °C (Ca(OH)₂ decomposition) is 7.29%. The results in Fig. 4 present that the decomposition weight loss of Ca(OH)₂ decreased from 7.29% to 5.46% and 4.65% after curing for 3 d and 28 d, indicating that HMPT-IOTs can directly react with Ca(OH)₂ to form C-S-H gel. The pozzolanic reactivity was attributed to its high SiO₂ content. It continues to dissolve during the hydration process and combines with CH to form C-S-H gel (Fang et al., 2024), resulting in a decrease in unreacted CH residues in the paste. At the same time, the weight loss in the range of 600 ~ 800 °C (CaCO₃ decomposition) decreased from 2.62% in 3 d to 1.98% in 28 d. CaCO₃ was mainly derived from the raw materials and the slight carbonation during the hydration process.

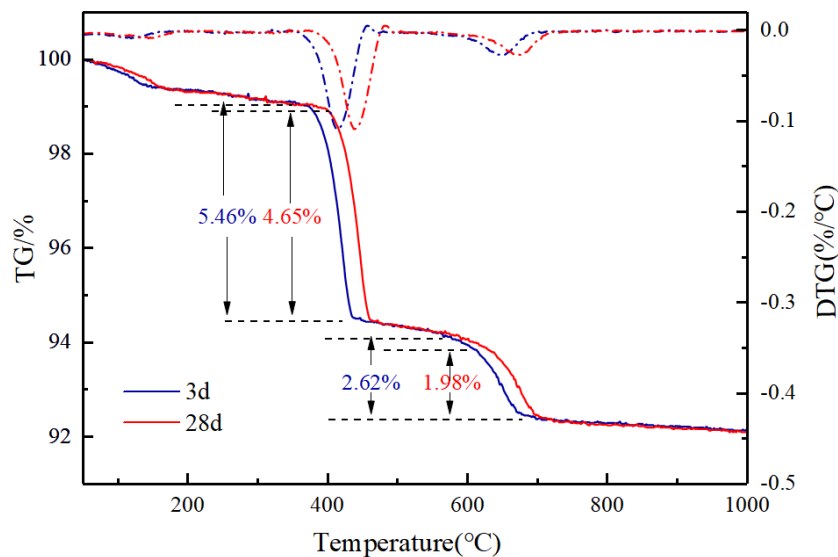


Fig. 4. HMPT-IOTs hydration 3 d, 28 d curves

3.2. Reaction characteristics of HMPT-IOTs in cementitious materials

3.2.1. Setting Time

The setting time of cement paste containing HMPT-IOTs is shown in Fig. 5. The results show that the initial setting time and final setting time of cement paste show a trend of prolongation with the increase

of HMPT-IOTs content, which indicates that HMPT-IOTs has a retarding effect on cement hydration. Notably, the cement paste incorporating 30% HMPT-IOTs exhibited the most pronounced prolongation in setting time, demonstrating setting characteristics of 362 min (initial) and 401 min (final). The incorporation of HMPT-IOTs dilutes the concentration of highly reactive cement particles in cement paste (Scrivener et al., 2018). And HMPT-IOTs participate negligibly in the early hydration reactions that drive setting (Yang et al., 2020). Thereby, this dilution effect directly reduces the content of active sites for the rapid formation of early hydration products, which are critical for building the cohesive skeleton of the paste. Beyond this dilution effect, the metastable Fe_3O_4 phase in HMPT-IOTs (30–45 wt%) actively contributes to hydration retardation through physicochemical interactions. This observation aligns with the kinetic model, which identified a compressed interface reaction (I) stage (Liu et al., 2023). Furthermore, the Fe_3O_4 particles may release $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions that can form surface complexes or precipitates on cement grains, slowing the early dissolution of C_3S and C_3A phases (Liu et al., 2023; Wang et al., 2023). Additionally, the fine Fe_3O_4 particles act as physical barriers and provide high-surface-area sites for Ca^{2+} adsorption, reducing the local supersaturation and lowering the early hydration intensity (Meng et al., 2025; Tang et al., 2024). This Fe_3O_4 -induced retardation is dosage-dependent and synergistic with the physical dilution effect, explaining the progressive prolongation of both initial and final setting times with increasing HMPT-IOTs content.

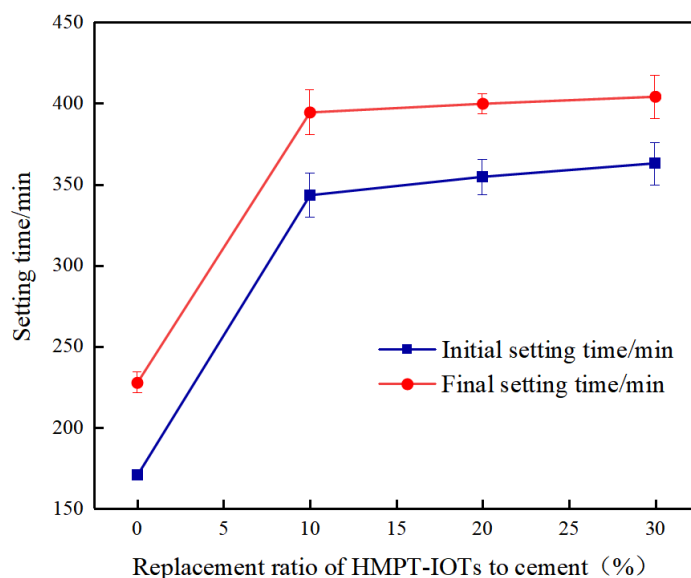


Fig. 5. Setting time of cement paste containing HMPT-IOTs

3.2.2. Chemically bound water content

The chemically bound water content, a key indicator of the hydration degree (Gu et al., 2021), was determined using the ignition loss method after 3 d and 28 d of curing, and the results are presented in Fig. 6. As indicated, the chemically bound water content exhibited an obvious decreasing trend with the increasing HMPT-IOTs content at both ages. When the HMPT-IOTs content was 10%, 20%, and 30%, the chemically bound water content decreased to 9.01%, 7.19%, and 6.54%, respectively, compared to 10.17% in the reference specimen. Similarly, at 28 d, the values decreased to 16.2%, 12.68%, and 11.89%, compared to 16.3% for the reference. This reduction is primarily attributed to the inherently low hydration reactivity of HMPT-IOTs. Unlike the cement clinker, which is highly reactive and rapidly forms substantial amounts of C-S-H gel and portlandite (CH), the iron tailings possess limited pozzolanic activity. Consequently, as HMPT-IOTs replace cement, the overall concentration of reactive components in the system is diluted. This leads directly to a lower total volume of hydration products and, hence, a decrease in chemically bound water. Therefore, the decline is more accurately explained by the dilution of reactive cementitious material and the low intrinsic reactivity of the tailings, rather than solely by an imbalance in calcium supply. This is consistent with the observed positive correlation between chemically bound water content and mechanical strength development, as both are fundamentally governed by the extent of hydration in the system.

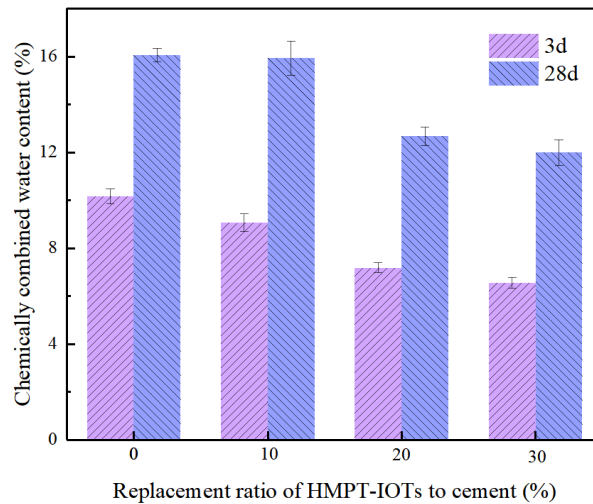


Fig. 6. Chemical bound water content of cement paste containing HMPT-IOTs

3.2.3. Hydration properties at early stage

As shown in Fig. 7, the incorporation of HMPT-IOTs induces a distinct bimodal pattern in the hydration heat release curve, which is closely associated with the transformation from AFt to AFm and the pozzolanic reaction (Meng et al., 2025). HMPT-IOTs provided additional nucleation sites, promoting early hydration reactions in the first hours, resulting in higher cumulative heat release in the composite cementitious materials compared to the reference specimen prior to 6 hours. Specifically, the 30% HMPT-IOTs replacement group exhibited the most pronounced retarding effect on cement hydration; and the second exothermic peak was delayed by 3.65 h relative to the reference specimen, and its peak height decreased by 30.2%. As a result, the cumulative heat during the first 72 h was reduced by 28.4%. Analogous trends were observed for the 10% and 20% HMPT-IOTs groups: their second exothermic peaks were delayed by 0.67 h and 0.45 h, respectively, with corresponding reductions in peak height of 13.6% and 18.6%; the respective 72 h cumulative heat releases declined by 5.9% and 15.7%. This retardation stems from two synergistic mechanisms. On the one hand, the partial replacement of cement clinker with inert HMPT-IOTs causes a dilution effect. On the other hand, the dispersed HMPT-IOTs particles act as a physical barrier, hindering the diffusion of water and hydrated ions. Together, they decelerate the overall hydration kinetics. However, as the HMPT-IOTs dosage increased, the height of the initial exothermic peak decreased, the peak onset time advanced, and the cumulative heat release after 6 hours was significantly reduced, indicating that high dosages inhibit the later stages of the hydration reaction. Therefore, HMPT-IOTs can promote early-stage hydration by providing reaction space and nucleation sites, but at high dosage levels, they weaken the intensity of later-stage reactions.

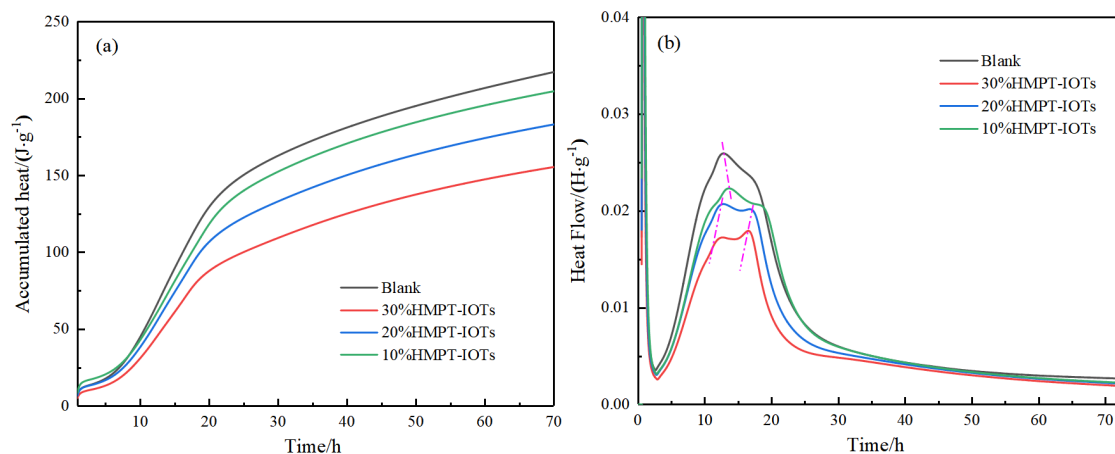


Fig. 7. Hydration heat of cement paste containing HMPT-IOTs: (a) cumulative hydration heat release curve, (b) hydration heat flow curve

The hydration of cement mainly divided into three basic processes: crystallization nucleation and crystal growth (NG), phase boundary reaction (I), and diffusion (D). The hydration degree data determined by experiment, and the kinetic equation given by the Krstulović-Dabić model (Chen et al., 2025) model is as follows to characterize the three stages of the hydration reaction of cement-based materials:

Crystallization nucleation and crystal growth stage (NG):

$$\frac{d\alpha}{dt} = F_1(\alpha) = K_1' n(1-\alpha)[- \ln(1-\alpha)]^{(n-1)/n} \quad (1)$$

Phase boundary reaction stage (I):

$$\frac{d\alpha}{dt} = F_2(\alpha) = K_2' 3(1-\alpha)^{2/3} \quad (2)$$

Diffusion stage (D):

$$\frac{d\alpha}{dt} = F_3(\alpha) = K_3' \cdot \frac{3}{2} (1-\alpha)^{2/3} / [1-(1-\alpha)^{1/3}] \quad (3)$$

In the formula: α is the degree of hydration; K_1' , K_2' and K_3' are the three stages of the hydration reaction stages; n is the reaction stage; t_0 is the end time of the induction period.

In addition, before solving the dynamic parameters such as K_1' , K_2' , K_3' , n , etc., the theoretical maximum heat release $Q_{\max}$ can be solved by formula (4); the degree of hydration α can be obtained from formula (5); $d\alpha/dt$ can be obtained from formula (6).

$$\frac{1}{Q(t)} = \frac{1}{Q_{\max}} + \frac{t_{50}}{Q_{\max}(t-t_0)} \quad (4)$$

$$\alpha = \frac{Q(t)}{Q_{\max}} \quad (5)$$

$$\frac{d\alpha}{dt} = \frac{dQ}{dt} \cdot \frac{1}{Q_{\max}} \quad (6)$$

In the formula: t_{50} is the time required for the hydration heat to reach 50%, that is, the half-life of the hydration reaction, h .

Fig. 8 presents the fitted hydration reaction rate curves for cement pastes incorporating varying contents of HMPT-IOTs. Notably, the kinetic parameters derived from these curves (Table 3) show a clear evolution in mechanism. The reduction in the reaction order n (from 1.62 to between 1.16 and 1.43) implies that growth becomes more spatially confined. We infer that the plentiful surfaces of the HMPT-IOTs particles are likely responsible for this shift.

The most significant kinetic impact is a marked redistribution of stage durations across the three canonical hydration phases. At 30 wt% substitution, the NG-to-I transition point (α_1) rises to 0.1672, which is about fivefold the control value of 0.0326, thereby indicating a pronounced extension of the nucleation and growth (NG) stage. In contrast, the duration of the intermediate interface reaction (I) stage, given by $(\alpha_2 - \alpha_1)$, contracts substantially from 0.1618 to 0.0626, reflecting a physical compression of this phase. It is particularly noteworthy that the apparent rate constant for the I stage (K_2') shows no statistical variation, confirming that the influence of HMPT-IOTs on this stage is predominantly physical rather than chemical.

What's more, the evolution of rate constants across different stages reveals distinct mechanistic roles, thereby offering additional support for this interpretation. The NG-stage rate constant (K_1') declines by ~50% at 30 wt% substitution, consistent with diminished linear growth efficiency per nucleation site—likely due to site proliferation and subsequent saturation. In contrast, the rate constant for the diffusion-controlled stage (K_3') increases by up to 85% at 20 wt% substitution. This suggests that the modified microstructure, resulting from the extended NG stage, enhances later-stage ion mobility and partially counteracts diffusion limitations.

Based on the kinetic modeling results, HMPT-IOTs do not just delay cement hydration but fundamentally reconfigure its early-stage progression. By introducing an abundance of heterogeneous nucleation sites, HMPT-IOTs transform the classical sequential pathway (NG $\rightarrow$ I $\rightarrow$ D) into a revised kinetic architecture: a protracted yet kinetically suppressed NG stage, a physically compressed I stage, and a diffusion stage exhibiting reduced resistance. This systemic reorganization of kinetic control provides a mechanistic foundation for the macroscopically observed retardation behavior.

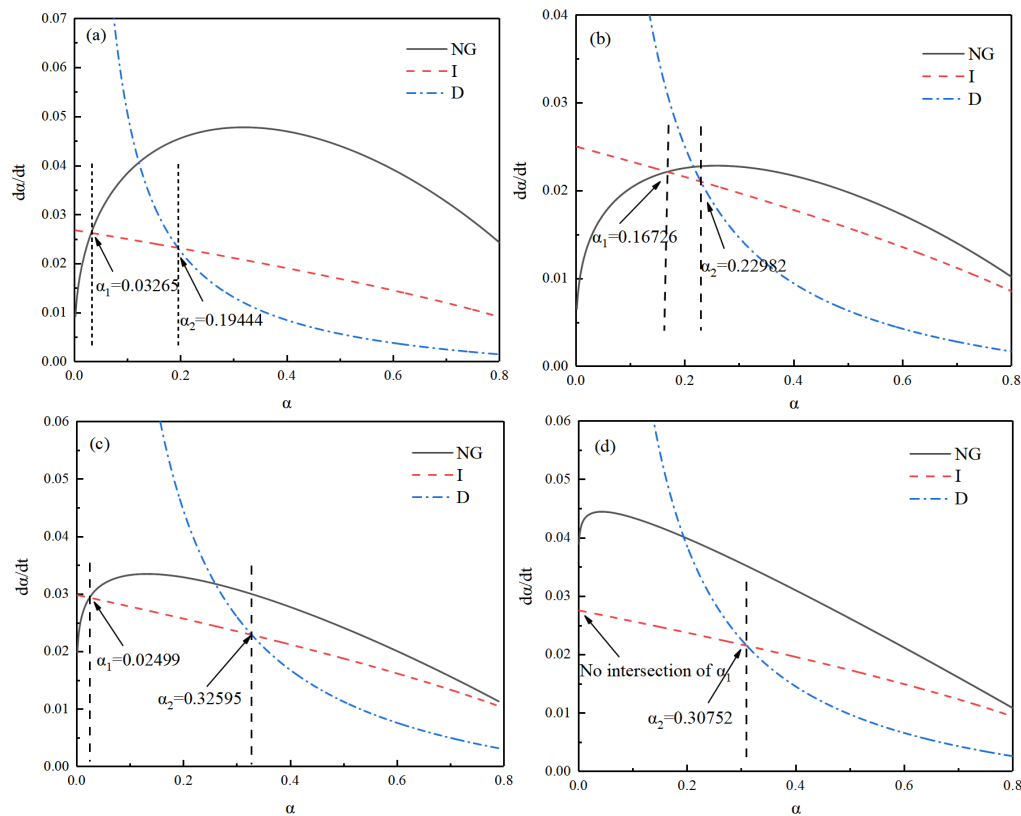


Fig. 8. The fitting curves of cement hydration rate: (a) Ref, (b) 30% HMPT-IOTs, (c) 20% HMPT-IOTs, (d) 10% HMPT-IOTs

Table 3. Hydration kinetic parameters of different gelling systems

Specimen	n	K_1'	K_2'	K_3'	Type	α_1	α_2	$\alpha_2 - \alpha_1$
Blank	1.6223	0.0625	0.0089	0.0013	NG-I-D	0.0326	0.1944	0.1618
30%HMPT-IOTs	1.4282	0.0310	0.0083	0.0013	NG-I-D	0.1672	0.2298	0.0626
20%HMPT-IOTs	1.1643	0.0437	0.0099	0.0024	NG-I-D	0.0249	0.3259	0.3010
10%HMPT-IOTs	1.2148	0.0464	0.0100	0.0018	NG-I-D	0.0281	0.2455	0.2174

3.2.4. Chemical shrinkage of cement paste at early stage

Chemical shrinkage is attributed to the reduction of absolute volume caused by the hydration reaction. As shown in Fig. 9, the overall chemical shrinkage of cement paste is significantly reduced with the incorporation of HMPT-IOTs. And this suppressing effect is positively correlated with the dosage. At an early stage (10 h), the shrinkage value of plain cement paste was 0.067, while pastes with 10%, 20%, and 30% HMPT-IOTs showed reduced values of 0.058, 0.065, and 0.059, respectively. By the end of the 176 h observation period, the cumulative shrinkage of plain cement reached 0.404, whereas the corresponding values for pastes with the aforementioned dosages were 0.369, 0.354, and 0.321, representing reductions of approximately 8.7%, 12.4%, and 20.5% compared to the control group. The data clearly demonstrate that higher dosages of HMPT-IOTs lead to greater suppression of chemical shrinkage.

In terms of the shrinkage development process, the chemical shrinkage curves of all groups exhibited multi-stage characteristics (Bouasker et al., 2008), but the slopes of the curves for pastes containing HMPT-IOTs were significantly lower in each stage. This is mainly attributed to the physical dilution effect and the slow hydration reactivity of HMPT-IOTs (Meng et al., 2025). As an admixture, HMPT-IOTs reduce the content of cement clinker per unit volume, directly decreasing the total amount of

reactants involved in early-stage rapid hydration. Simultaneously, their own hydration reaction is slow, making it difficult to effectively form hydration products in the early stage, thereby lowering the overall degree of hydration in the system and delaying the nucleation and growth of products such as C-S-H. This is consistent with the conclusion from previous studies that HMPT-IOTs prolong the setting time, collectively indicating their significant retarding effect on early hydration. Furthermore, Fe_3O_4 particles can reduce the effective water available for hydration and delay the Aft-to-AFm transition, both of which suppress chemical shrinkage beyond the dilution effect.

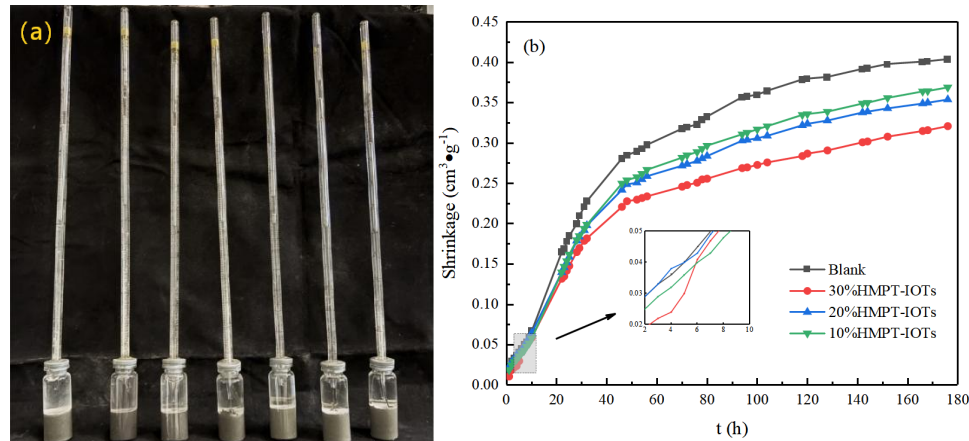


Fig. 9. Chemical shrinkage cement pastes containing HMPT-IOTs: (a) Appearance of the test sample, (b) Chemical shrinkage curves

3.3. Compressive strength of mortar

The 3 d and 28 d compressive and flexural strengths of mortars incorporating HMPT-IOTs are summarized in Fig. 10. As anticipated, both compressive and flexural strengths exhibited a progressive decline with increasing HMPT-IOTs content (Gu et al., 2022). This trend can be attributed to the cement dilution effect and the inherent low pozzolanic reactivity of HMPT-IOTs during the 28 d curing period (Meng et al., 2025). Strength loss was more pronounced at early ages. While a 30% replacement caused a sharp 55.4% drop in 3 d compressive strength (from 34.1 to 15.2 MPa), its impact on the 28 d strength was more moderate, with a 44.1% reduction (from 58.9 to 32.9 MPa). The sluggish reaction kinetics of HMPT-IOTs, consistent with the extended nucleation phase seen in models, explains this disparity. It fundamentally limits their contribution to early-age strength development (Li et al., 2022). Another factor requiring careful consideration is the strength retention efficiency – a ratio quantifying how much 28 d compressive strength is gained per unit mass of cement replaced. When replacement increased from 10% to 20%, the 28 d compressive strength retention dropped non-linearly from 73.1% to 67.3%. This sharpening decline points to 10% as a critical threshold before accelerated deterioration sets in. Separately, the slight rise in the flexural-to-compressive strength ratio at 28 d with HMPT-IOTs hints at a possible change in material behavior, potentially leading to less brittle fracture (Li et al., 2023).

Although the replacement of HMPT-IOT will inevitably reduce mechanical properties due to cement dilution and limited reactivity, according to a comprehensive mechanical evaluation, the recommended maximum replacement ratio is 10%. This dose achieves the best compromise between sustainable solid waste utilization and structural integrity protection, while reducing the adverse impact of changes in hydration dynamics on early force development (Gou et al., 2019). The superior strength retention at this optimal 10% replacement is consistent with SEM observations of a refined ITZ and dense C-S-H coating, confirming that microstructural densification directly translates to macro-mechanical performance.

3.4. Microstructural evolution and phase analysis

3.4.1. Morphology and microstructure (SEM)

For the paste containing 20% HMPT-IOTs, SEM characterization (Fig. 11) indicated that the plain cement paste after 3 d was mainly composed of acicular Aft, platy CH, and nascent C-S-H gel. These phases

formed in a dispersed arrangement, leading to a microstructure with noticeable porosity and interparticle voids.

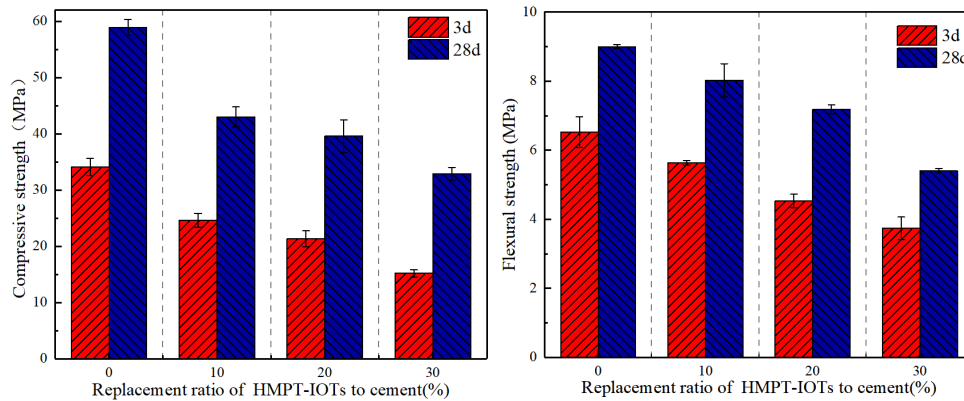


Fig. 10. The compressive strength and flexural strength of HMPT-IOTs

The paste with HMPT-IOTs (Fig. 11 (b)) exhibited a fundamentally different microstructure. A key feature was the rough, heterogeneous surface of the tailing's particles, which functioned as active sites for heterogeneous nucleation (Meng et al., 2025). This facilitated a denser and more uniform distribution of early hydration products (C-S-H gel and Aft), promoting early microfilling and enhanced matrix continuity. Thus, the SEM observations provide direct microstructural support for the extended nucleation and growth (NG) stage identified in kinetic modeling (Tang et al., 2024), confirming the operative “heterogeneous nucleation” mechanism.

After 28 d of maintenance (Fig. 12), the microstructure of the two hydrated slurry shows a denser phenomenon. In slurry containing HMPT-IOTs, the gel phase (including C-S-H and possible carbon aluminum silicate hydrate (C-A-S-H)) shows stronger interconnectivity. Over time, the limited volcanic ash reaction is likely to continue, resulting in a complementary gel phase, which contributes to pore

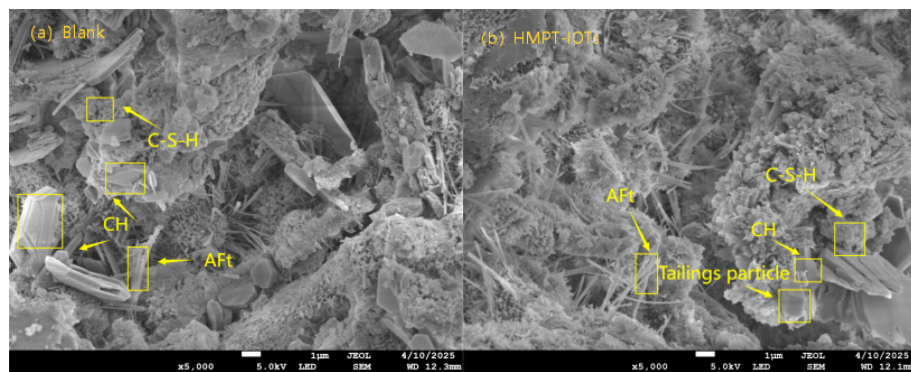


Fig. 11. SEM images of different hydrated 3 d samples: (a) Blank; (b) HMPT-IOTs

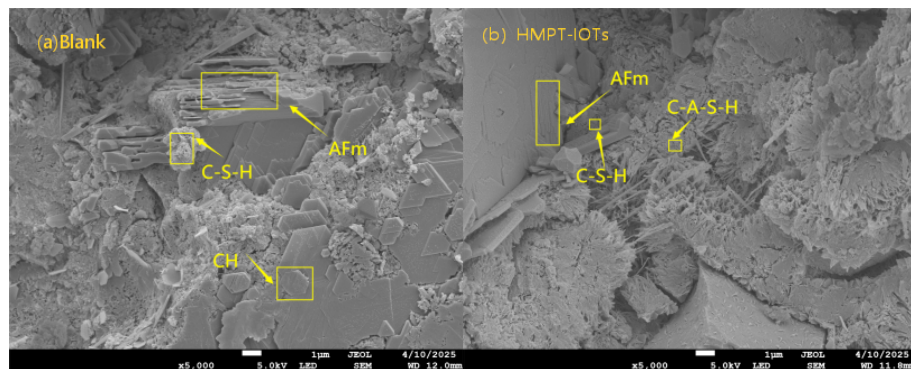


Fig. 12. SEM images of different hydrated 28 d samples: (a) Blank; (b) HMPT-IOTs

refinement and improves the integrity of the interface transition zone (ITZ) between the tailings particles and the surrounding gelling matrix.

These microstructural characteristics directly explain the macroscopic mechanical behavior. Specifically, at 10% replacement, the denser ITZ and more uniform distribution of hydration products effectively mitigate stress concentration and microcrack propagation, which underpins the observed 73.1% retention of 28 d compressive strength and the flexural strength comparable to pure cement. At 30% replacement, however, the limited pozzolanic activity fails to fully densify the ITZ, leading to a weaker matrix–aggregate bond and a pronounced strength loss (44.1% reduction at 28 d). Thus, the correlation between ITZ densification and strength retention is dosage-dependent: low HMPT-IOTs content enhances interfacial bonding via heterogeneous nucleation, while high content leaves the ITZ partially porous due to insufficient pozzolanic gel formation. This observation aligns with the kinetic model, which identified a compressed interface reaction (I) stage, confirming that HMPT-IOTs function primarily as inert physical substrates that promote early heterogeneous nucleation and refine initial microstructure, but their inherently low hydraulic and pozzolanic reactivity cannot compensate for the quantitative loss of cement-derived binding phases (Li et al., 2022).

3.4.2. Thermal decomposition and phase quantification (TG-DTG)

The influence of HMPT-IOTs on the composition of hydration products and its evolution over time were tested based on the TG-DTG analysis at 3 and 28 d (Fig. 13 and Fig. 14). TG analysis quantitatively confirms that with the increase of HMPT-IOTs dosage from 0% to 30%, the decomposition of C-S-H gel (mass loss at 100 ~ 200 °C) progressively decreased from 9.74% to 7.50% (a reduction of 23.0%), and portlandite (CH, mass loss at 400 ~ 450 °C) decreased from 12.25% to 8.98% (a reduction of 26.7%) at 3 d. The reduction in CH at this stage was mainly attributed to the dilution of cement clinker, while the decomposition loss of C-S-H was relatively less pronounced. This observation aligns with the SEM findings of C-S-H enrichment on tailings particle surfaces and the prolonged nucleation-and-growth period in the hydration kinetics (Meng et al., 2025), indicating that the high surface area of the tailings provides abundant sites for heterogeneous nucleation, locally promoting C-S-H precipitation and partially offsetting the decrease in gel content caused by dilution.

By 28 d, the reaction mechanism had shifted significantly, with clear signs of pozzolanic activity. The CH content saw a further decline. In the 30% mixture, it reached 8.56%, which is 32.7% lower than the blank sample (12.71%). This reduction is more pronounced than the 26.7% drop at 3 d and surpasses the level attributable to mere dilution, confirming that pozzolanic reactions between HMPT-IOTs and CH had begun (Yao et al., 2020). Concurrently, the C-S-H/C-A-S-H gel content rebounded substantially. For the 30% mixture, it increased from 7.50% at 3 d to 14.87% at 28 d, bringing it close to the blank sample's level of 15.74%. This recovery suggests that ongoing hydration (promoted by nucleation sites) and the new pozzolanic gels collectively made up for the early strength loss due to cement replacement.

The evolving product composition provides a clear explanation for the pattern of strength development (Li et al., 2023; Meng et al., 2025). Early-age (3 d) behavior was dominated by physical filling, while later-age (28 d) performance showed definite pozzolanic activity. This shift accounts for the observed moderation in strength loss at later ages. For instance, at 30% replacement, the compressive strength loss narrowed from 55.4% to 44.1%. However, by 28 d, the amount of gel generated through these slow pozzolanic reactions at high replacement levels remains inadequate to fully overcome the dominant cement dilution effect (Gu et al., 2022).

4. Conclusions

Investigating the hydration, strength development, and microstructure of hydrogen-based mineral phase transformation iron ore tailings (HMPT-IOTs) as a low-carbon SCM, this work employed comprehensive characterization techniques. These included XRD, SEM, TG-DTG, isothermal calorimetry, and mechanical testing at 10%, 20%, and 30% replacement levels. This led to the following conclusions.

- (1) HMPT-IOTs exhibit a dual role in cement hydration: they act as effective heterogeneous nucleation sites via their rough surfaces, significantly extending the nucleation-and-growth stage by up to 5-fold, yet their intrinsically low and slow-developing pozzolanic reactivity

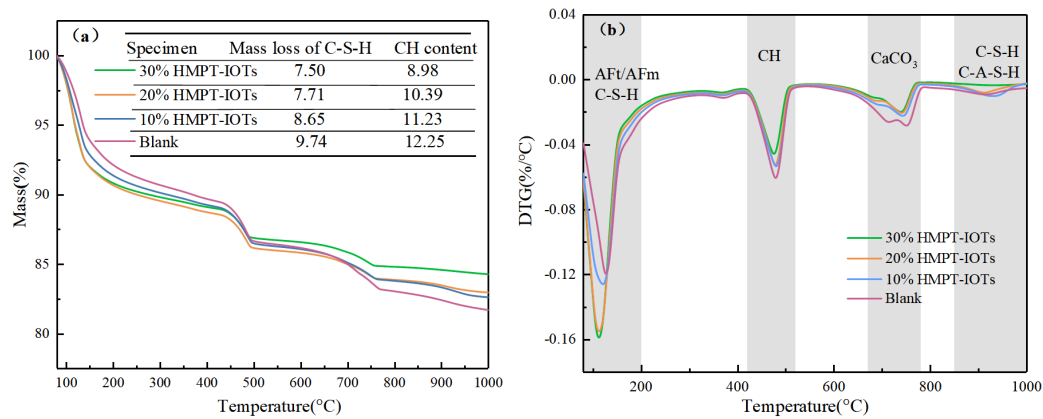


Fig. 13. Curves of different HMPT-IOTs content hydrated for 3 d: (a) TG curves, (b) DTG curves

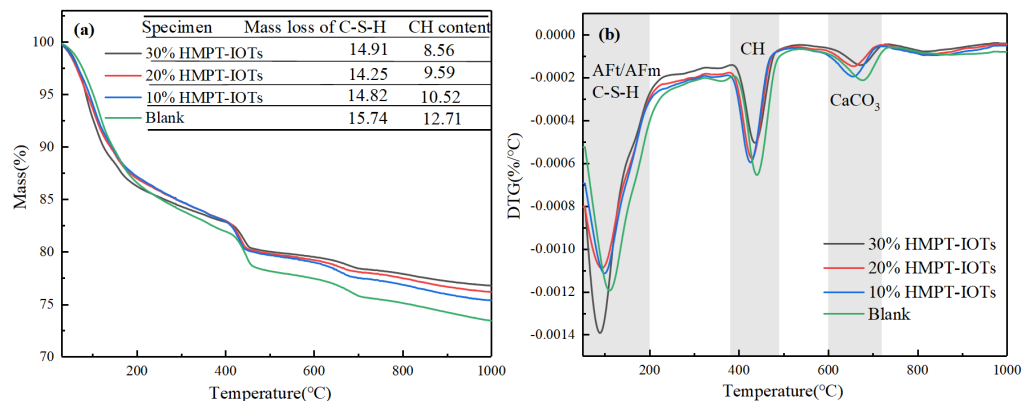


Fig. 14. Curves of different HMPT-IOTs content hydrated for 28 d: (a) TG curves, (b) DTG curves

limits long-term strength compensation. This previously unrecognized kinetic transition is the key novelty of this work, which reconfigures the canonical cement hydration pathway from chemically-driven to diffusion-limited control.

- (1) The optimal replacement dosage is identified as ≈ 10 wt%. At this level, early-age microstructural densification via C-S-H nucleation effectively offsets cement dilution, preserving mechanical integrity (28 d compressive strength retention of 73.1%) while refining the interfacial transition zone. By 28 d, pozzolanic activity emerges, evidenced by up to 32.7% portlandite consumption and additional C-S-H gel formation.
- (2) Higher replacement levels (≥ 20 wt%) lead to pronounced strength loss due to insufficient pozzolanic gel formation, demonstrating that the nucleation effect cannot substitute for cement-derived binding phases beyond a critical threshold. At 30 wt% replacement, the dominant dilution effect causes a 44.1% reduction in 28 d compressive strength.
- (3) Using 10% HMPT-IOTs as SCM reduces cement consumption and associated CO_2 emissions by approximately 8–10% per ton of cementitious material while valorizing an otherwise landfilled industrial solid waste. This offers a viable and scalable pathway for low-carbon construction materials.
- (4) Limitations and prospects: This study focuses on hydration performance and mechanical properties up to 28 d; long-term durability (e.g., carbonation, chloride penetration, freeze-thaw resistance) and environmental safety (e.g., heavy metal leaching) require further systematic investigation. Future work should also explore targeted activation methods (e.g., ultra-fine grinding or chemical activators) to enhance the pozzolanic reactivity of HMPT-IOTs for higher replacement ratios.

Acknowledgements

This work was financed by National Natural Science Foundation of China (U23A20603), Hainan Province Science and Technology Special Fund, China (ZDYF2025GXJS196), Liaoning Province Natural

Science Foundation, China (2025-BS-0478), Liaoning Revitalization Talents Pro-program (XLYC2503133) and Scientific Research Foundation of Liaoning Provincial Education Department, China (LJ222610153003).

References

- AMJAD H., ELAAL E.S.A., MA X. et al., 2025. *A critical review of iron ore tailings as cement and aggregate substitutes for robust infrastructure: mechanical, durability, eco-economic, and social impacts*. Journal of Cleaner Production, 492: 144853.
- BOUASKER M., MOUNANGA P., TURCRY P. et al., 2008. *Chemical shrinkage of cement pastes and mortars at very early age: effect of limestone filler and granular inclusions*. Cement and Concrete Composites, 30: 13–22.
- CHAO X., HAN C., SHAO C. et al., 2024. *Recent advances in properties and application progress of cement-based materials with iron tailing*. Sustainability, 16: 10631.
- CHEN J., XIE B., LU Z. et al., 2025. *Early hydration characteristics and kinetics model of ordinary Portland cement-calcium sulfoaluminate cement composites*. Materials, 18: 2559.
- CHEN L., TANG Y., 2025. *Analysis of the influence of iron tailings sand on the properties of concrete mixtures and cyclic compressive behavior*. Scientific Reports, 15: 26857.
- DUAN P., YAN C., ZHOU W. et al., 2016. *Fresh properties, compressive strength and microstructure of fly ash geopolymers paste blended with iron ore tailing under thermal cycle*. Construction and Building Materials, 118: 76–88.
- FANG Y., QIAO L., HU T. et al., 2025. *Characteristics of iron ore tailings sand and properties of iron ore tailings sand concrete: a review*. International Journal of Concrete Structures and Materials, 19: 41.
- FANG Y., SHAN J., WANG Q. et al., 2024. *Semi-dry and aqueous carbonation of steel slag: characteristics and properties of steel slag as supplementary cementitious materials*. Construction and Building Materials, 425: 135981.
- GOU M., ZHOU L., THEN N.W.Y., 2019. *Utilization of tailings in cement and concrete: a review*. Science and Engineering of Composite Materials, 26: 449–464.
- GU C., YANG J., YANG Y. et al., 2021. *The relationship of compressive strength and chemically bound water content of high-volume fly ash-cement mortar*. Materials, 14: 6273.
- GU X., LIU B., LI Z. et al., 2023. *Mechanical grinding kinetics and particle packing novel characterization of iron ore tailings as inert filler for cement mortar*. Journal of Building Engineering, 78: 107558.
- GU X., ZHANG W., ZHANG X. et al., 2022. *Hydration characteristics investigation of iron tailings blended ultra-high-performance concrete: the effects of mechanical activation and iron tailings content*. Journal of Building Engineering, 45: 103459.
- GURSEL A.P., MASANET E., HORVATH A. et al., 2014. *Life-cycle inventory analysis of concrete production: a critical review*. Cement and Concrete Composites, 51: 38–48.
- HAN X., WANG F., ZHAO Y. et al., 2022. *Recycling of iron ore tailings into magnetic nanoparticles and nanoporous materials for the remediation of water, air and soil: a review*. Environmental Chemistry Letters, 21: 1005–1028.
- KINNUNEN P.H.M., KAKSONEN A.H., 2019. *Towards circular economy in mining: opportunities and bottlenecks for tailings valorization*. Journal of Cleaner Production, 228: 153–160.
- KURANCHIE F.A., SHUKLA S.K., HABIBI D. et al., 2015. *Utilisation of iron ore tailings as aggregates in concrete*. Cogent Engineering, 2: 1083137.
- LI H.W., WANG R., WANG M.W. et al., 2022. *Mechanical properties and hydration mechanism of high-volume ultra-fine iron ore tailings cementitious materials*. Construction and Building Materials, 353: 129100.
- LI J., REN W., ZHANG A. et al., 2023. *Mechanical properties and microstructure analysis of cement mortar mixed with iron ore tailings*. Buildings, 13: 149.
- LIU K., WANG S., QUAN X. et al., 2023. *Development of engineered cementitious composites (ECCs) incorporating iron ore tailings as eco-friendly aggregates*. Buildings, 13: 1341.
- LIU X., XU H., LI B. et al., 2023. *Investigation of the mechanical properties of iron tailings concrete subjected to dry-wet cycle and negative temperature*. Materials, 16: 4602.
- MENG X., TANG Z., GAO P. et al., 2025. *Mechanism analysis of hydrogen mineral phase-transformed iron ore tailings in cementitious materials: a study on hydration kinetics, mechanical properties, and microstructural characteristics*. Construction and Building Materials, 475: 141260.
- MOAFAK M.A., MUWAFFAQ A., ALI M. et al., 2022. *Concrete made with iron ore tailings as a fine aggregate: a step towards sustainable concrete*. Materials, 15: 6236.

- NING J., GAO P., WANG Y. et al., 2025. Mineralogical characterization and flotation properties of rare earths in refractory iron tailings subjected to hydrogen-based mineral phase transformation. *International Journal of Minerals, Metallurgy and Materials*, 32: 1309–1321.
- NING J., GAO P., YUAN S. et al., 2024. Green approach for separating iron and rare earths from complex polymetallic solid residues via hydrogen-based mineral phase transformation: a pilot-scale study. *Separation and Purification Technology*, 350: 128006.
- RUSO F., ORETO C., VEROPALUMBO R., 2022. Promoting resource conservation in road flexible pavement using jet grouting and plastic waste as filler. *Resources, Conservation and Recycling*, 187: 106633.
- SCRIVENER K.L., JOHN V.M., GARTNER E.M., 2018. Eco-efficient cements: potential economically viable solutions for a low-CO₂ cement-based materials industry. *Cement and Concrete Research*, 114: 2–26.
- SUI S., ZHAO Y., HAI L. et al., 2024. Laboratory investigation on the bioremediation technology for soilization of iron ore tailings. *Scientific Reports*, 14: 27966.
- TANG Z., LI P., GAO P. et al., 2022. Minerals phase transformation by hydrogen reduction technology: a new approach to recycle iron from refractory limonite for reducing carbon emissions. *Advanced Powder Technology*, 33: 103870.
- TANG Z., MENG X., HAN Y. et al., 2024. Hydration and properties of hydrogen-based mineral phase transformation iron ore tailings as supplementary cementitious material. *Journal of Environmental Management*, 356: 120594.
- TIAN P., GAO P., WANG M. et al., 2025. Pilot-scale recovery of iron from refractory specularite ore using hydrogen-based mineral phase transformation technology: process optimization, mineral characterization, and green production. *Journal of Cleaner Production*, 491: 144836.
- WANG C., HARBOTTLE D., LIU Q. et al., 2014. Current state of fine mineral tailings treatment: a critical review on theory and practice. *Minerals Engineering*, 58: 113–131.
- WANG H., GU X., LIU J. et al., 2023. Enhancement mechanism of micro-iron ore tailings on mechanical properties and hydration characteristics of cement-steel slag system. *Journal of Building Engineering*, 79: 107882.
- WANG R., YUAN S., LI Y. et al., 2024. Hydrogen-based mineral phase transformation mechanism investigation of pyrolusite ore. *International Journal of Minerals, Metallurgy and Materials*, 31: 2445–2457.
- WU Z., DENG J., ZHAO T. et al., 2024. Transforming mining waste to wealth: a novel process for the sustainable recovery and utilization of iron tailings through HCl leaching and MOFs absorption. *Sustainability*, 16: 1945.
- YANG G., XIE Q., LI Y. et al., 2024. Mineralogy and geochemistry of iron tailings from Yeshan iron deposit, Southwest Jiangsu, China: implications for potential utilization. *ACS Omega*, 9: 3827–3834.
- YANG M., SUN J., DUN C. et al., 2020. Cementitious activity optimization studies of iron tailings powder as a concrete admixture. *Construction and Building Materials*, 265: 120760.
- YAO G., LIU Q., WANG J. et al., 2019. Effect of mechanical grinding on pozzolanic activity and hydration properties of siliceous gold ore tailings. *Journal of Cleaner Production*, 217: 12–21.
- YAO G., WANG Q., WANG Z. et al., 2020. Activation of hydration properties of iron ore tailings and their application as supplementary cementitious materials in cement. *Powder Technology*, 360: 863–871.
- ZHANG C., LI S., 2018. Utilization of iron ore tailing for the synthesis of zeolite A by hydrothermal method. *Journal of Material Cycles and Waste Management*, 20: 1605–1614.
- ZHANG J., HAN Y., LI Y. et al., 2025. An efficient and clean method for iron extraction from refractory hematite using hydrogen-based mineral phase transformation. *JOM*, 77: 1–15.
- ZHANG T., GAO P., LUO R. et al., 2013. Measurement of chemical shrinkage of cement paste: comparison study of ASTM C 1608 and an improved method. *Construction and Building Materials*, 48: 662–669.
- ZHANG Y., YANG D., GU X. et al., 2022. Application of iron tailings-based composite supplementary cementitious materials (SCMs) in green concrete. *Materials*, 15: 3866.
- ZHAO N., QIU Y., QI S. et al., 2025. Hydrogen-assisted mineral phase transformation for iron recovery and sulfur removal from laterite nickel ore tailings. *International Journal of Minerals, Metallurgy and Materials*, 32: 2429–2443.

