

Synergistic effect of DTPA-5Na and FGD gypsum on basic oxygen furnace slag-based cementitious materials

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ABSTRACT

Basic oxygen furnace (BOF) slag remains underutilized due to its low reactivity. This study introduces a novel activation method combining pentasodium diethylenetriamine pentaacetate (DTPA-5Na) with flue gas desulphurization (FGD) gypsum to enhance slag dissolution and hydration. The advantages of the synergistic activation of BOF slag were assessed through mineralogical, thermal, and microstructural analyses. Results reveal that 1.0 wt% DTPA-5Na effectively boosts brownmillerite and belite reactivity through the chelation process, accelerating monocarboaluminate and C-S-H gel formation and raising compressive strength by 140% at 28 d. Synergistic use of FGD gypsum regulates calcium and sulphate release, promoting ettringite and hydrocalumite formation while reducing porosity by 31%. The binder achieves 35.8 MPa compressive strength (28 d) while meeting Dutch Soil Quality Decree leaching limits. The addition calcium can retard the hydration process, while the strength performance is related to the sulphate content. The developed hydration model indicates low water demand (0.22–0.26, water-to-binder_{slag}) and superior volume stability (chemical shrinkage 2.0–3.5 ml/100 g_{slag}) of BOF slag-based cementitious materials. These findings support the sustainable valorisation of BOF slag through low-dosage chelator activation combined with the concurrent recycling of sulphate-bearing industrial waste.

1. Introduction

The cement industry accounts for approximately 8% of global anthropogenic CO₂ emissions, underscoring the necessity of developing alternative materials to support low-carbon, resource-efficient and circular economy goals [1–4]. Basic oxygen furnace (BOF) slag, a solid by-product of the steelmaking industry, has garnered growing attention as a potential cementitious material [5,6]. It is produced in quantities of approximately 90–100 kg per ton of steel during the refinement of pig iron into crude steel, resulting in an annual production of about 10.4 million tons in Europe [4,7]. Mineralogically, BOF slag contains phases, such as alite, belite, brownmillerite, lime, magnetite and wüstite [6,8], indicating its latent hydraulic potential. However, its application remains limited, typically used at up to 5% replacement in OPC systems and 30–50% in belite calcium sulphaaluminate cement, due to its low alite content (0–5 wt%) and high belite content (40–55 wt%) [9,10]. Consequently, a substantial portion of BOF slag remains underutilized, highlighting the need for further research into strategies to enhance its reactivity and performance.

Due to the high belite content in BOF slag, its hydraulic activity is limited at the early stages of hydration [11]. Previous research efforts have primarily focused on enhancing belite hydration through mechanical grinding and chemical activation using alkali hydroxides, salts (e.g., CaCl₂, Na₂CO₃, Na₂SiO₃), and boron-bearing dopants [12–16]. Nevertheless, their effectiveness remains limited. One explanation is the precipitation of calcium silicate hydrate (C-S-H) and calcite on belite surface, which impedes further hydration by restricting cations transport [17]. Recently, Yong et al. elucidated the dissolution mechanism of dicalcium silicate through molecular dynamics and kinetic Monte Carlo (KMC) simulations [18]. Dissolution proceeds via sequential Ca detachment, the rate-limiting step being the breaking of the first Ca-Osi/Ohs bond and its conversion into a Ca-Ow/Oh bond. In addition, the dissolution rate is strongly affected by the saturation state of the pore solutions. Based on these insights, this study proposes to improve BOF slag reactivity through promoted mineral dissolution, facilitated by formation of stable coordination complexes between chelators and the dissolved ions such as Ca²⁺, Al³⁺, and Fe³⁺ that commonly released from slag phases.

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Chelating agents, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and oxalate, contain multiple coordination atoms (sites) that enable stable complexation with metal ions [19–21]. Owing to their strong binding ability, chelating agents are widely used for metal stabilization, extraction, and dissolution of metal salts. For instance, EDTA boosts the dissolution rate of calcite by up to one order of magnitude compared to systems without EDTA [22]. Recent studies have explored chelators for activating BOF slag; Chang et al. showed that ethanol-diisopropanolamine (EDIPA) accelerates the hydration via chelation with Ca^{2+} , Al^{3+} and Fe^{3+} ions [23]. However, despite this acceleration, the resulting mechanical performance of the formulated BOF slag-based pastes remained low (around 4.5 MPa at 28 d), limiting its application as a promising substitute for Portland cement. Improved strength has been achieved at a lower w/b ratio (0.16–0.18) using tri-potassium citrate monohydrate and di-sodium oxalate, owing to their superplasticizing effects that enables desirable workability [6,24]. These studies have demonstrated the potential of chelators for activating BOF slag as construction materials. Theoretically, this enhanced activation could be partially attributed to the increased Ca-coordination through chelation, which reduces free Ca^{2+} activity in the pore solution and thereby facilitates the dissolution of hydraulically reactive phases. However, effective activation often requires high dosage of chelators, (e.g., EDTA–4Na at 4.8 wt% and di-sodium oxalate at 3 wt% [21,24]), which significantly increases costs and limits practical applicability. The demand for high chelator content is partly attributed to the relatively low coordination capacity of used chelators. The typical denticity of citrate-, EDTA- and oxalate- based chelators is 3, 6 and 2, respectively. Higher denticity generally enhances metal-ligand complexation; for instance, DTPA–5Na, with 8 donor atoms, exhibits stronger coordination capacity. Lindsay & Norvell developed a DTPA-based extraction method to estimate plant-available micronutrients, including Zn, Fe, Mn, and Cu, in near-neutral and calcareous soils [25]. Owing to its strong chelating capacity for polyvalent metal cations, DTPA has since been employed across a broad range of fields, including water treatment, food processing, textiles, and medical detoxification [26,27]. However, its application in cementitious and slag-based materials remains largely unexplored. Herein, this study proposes the use of DTPA–5Na (<1 wt%) to achieve efficient activation of BOF slag while improving cost effectiveness and scalability.

In addition, chelation efficiency may be constrained by ion saturation during early hydration, as continuous ion release can occupy available coordination sites. Thus, reducing ions saturation offers an alternative strategy to enhance chelation. In BOF slag, brownmillerite (~20 wt%) plays a key role as a solid solution with the formula $\text{Ca}_2(\text{Al}_x\text{Fe}_{2-x})\text{O}_5$, releasing Ca^{2+} , Al^{3+} and Fe^{3+} ions during early hydration. In Portland cement, it typically appears as $\text{Ca}_2\text{FeAlO}_5$. Its hydration occurs in the early stages and leads to the formation of Fe-containing Afm phase and hydrogarnets [28,29]. Upon exposure to water, brownmillerite initially forms a metastable gel identified as C-(A, F)-H, which gradually transforms into hydrogarnet phases over time [30,31]. However, its hydraulic activity diminishes as the iron content increases [32], and the iron-rich brownmillerite present in BOF slag is expected to exhibit reduced hydraulic activity, thereby restricting strength development. The incorporation of chelating agents may accelerate the dissolution of brownmillerite, promoting the release of Ca^{2+} , Al^{3+} and Fe^{3+} ions. Nevertheless, it is important to note that the dissolution rate of C_2S could be further hindered under conditions of high Ca^{2+} saturation in the pore solution [18]. To address this, additional sulphates (gypsum and sodium sulphate) are introduced in this study to facilitate ettringite formation [33], which are expected to reduce Ca^{2+} saturation, thereby promoting the dissolution of both C_2S and brownmillerite. Nonetheless, these proposed mechanisms remain hypothetical in the absence of a comprehensive investigations of the interactions between chelating agents and BOF slag minerals.

Herein, we develop a new strategy that considers both Ca-coordination and calcium saturation to enhance the performance of

BOF slag-based cementitious materials. DTPA–5Na is employed to improve Ca-coordination through chelation, thereby reducing free ion activity and enhancing the dissolution of reactive minerals in BOF slag. To regulate calcium ion saturation, sulphate is then introduced via FGD gypsum. The role of calcium and sulphate ions is revealed in comparison with sodium sulphate. The effect of DTPA–5Na and gypsum on hydration kinetics, phase assemblage, and microstructure are systematically investigated to elucidate the mechanisms underlying improved performance. Furthermore, a hydration model of BOF slag-based cementitious materials activated with DTPA–5Na and FGD gypsum is developed based on the hydration process of BOF slag, accompanied by a theoretical assessment of volume stability. The findings demonstrate a sustainable pathway for high-volume utilization of BOF slag and the recycling of sulphur-rich industrial residues into BOF slag-based cementitious materials.

2. Materials and methods

2.1. Materials

Two types of raw materials, BOF slag and FGD gypsum, were used in the preparation of pastes. BOF slag was supplied by Tata Steel (IJmuiden, The Netherlands). The received BOF slag with a size of < 5.6 mm was stored in air-tight plastic drums to prevent carbonation. In order to apply the BOF slag as a binder material, it was further ground using a Retsch RS 300 XL disc mill at a speed of 912 min^{-1} for 15 min. FGD gypsum was collected from a coal-combustion power plant. All the raw materials were vacuum-dried at 60°C for one day to remove the moisture content. DTPA–5Na, purchased from Sigma Aldrich (CAS 140–01–2, 40% aqueous solution), was used as the activator of the BOF slag. The chemical structure of DTPA–5Na is presented in Fig. 1. Sodium sulphate, sourced from Sigma Aldrich (CAS 7757–8582–6, $\geq 99.0\%$), was used in comparison with FGD gypsum.

The chemical composition of raw materials was determined by X-ray Fluorescence analysis (XRF, PANalytical Epsilon 3) using a fused bead method, and the results are given in oxide weight percentages in Table 1. The BOF slag mainly comprises CaO , Fe_2O_3 , SiO_2 , MgO and MnO . Notably, all Fe in the BOF slag is reported as Fe_2O_3 ; but Fe can occur in the form of Fe^0 , Fe^{2+} , and Fe^{3+} in the BOF slag. The oxidation of metallic or divalent iron leads to increased mass when the BOF slag is heated up to 1000°C for the loss on ignition (LOI) test, also observed in [34]. Meanwhile, the mineralogical composition of the raw materials was investigated on Bruker D4 diffractometer with $\text{CoK}\alpha$ radiation. Reflections were measured in a 2 Theta (2θ) range of 10° to 60° with a step size of 0.02° . The phase identification was conducted with Highscore Plus using the ICDD PDF–2 database. The main phases in BOF slag, as shown in Fig. 2, are $(\alpha' + \beta)$ C_2S , wüstite, magnetite, and brownmillerite. A high concentration of gypsum ($\geq 95\%$) is also confirmed in the FGD gypsum. The particle size distribution of the milled BOF slag and FGD gypsum was characterized using a Mastersizer2000 from Malvern, as illustrated in Fig. 3. Isopropanol was used as the solvent during the measurement to prevent the dissolution or hydration reaction. The $d(50)$ of the milled BOF slag and FGD gypsum are 15.4 and $31.9\text{ }\mu\text{m}$, respectively.

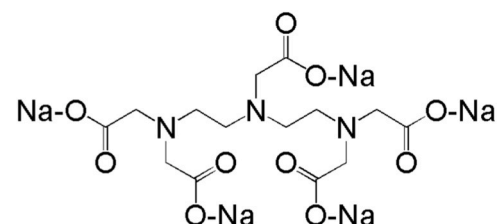


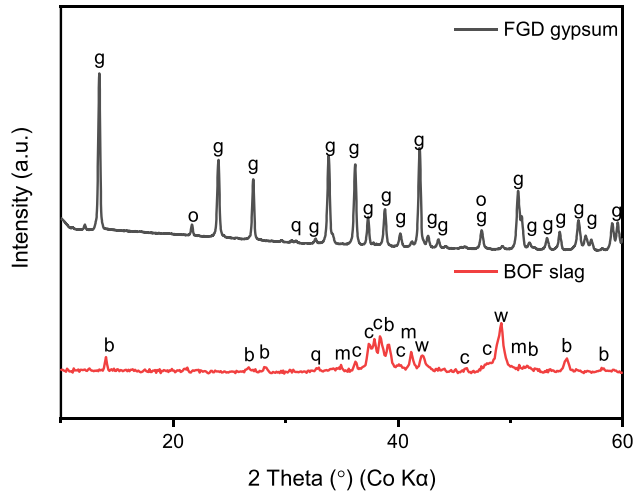
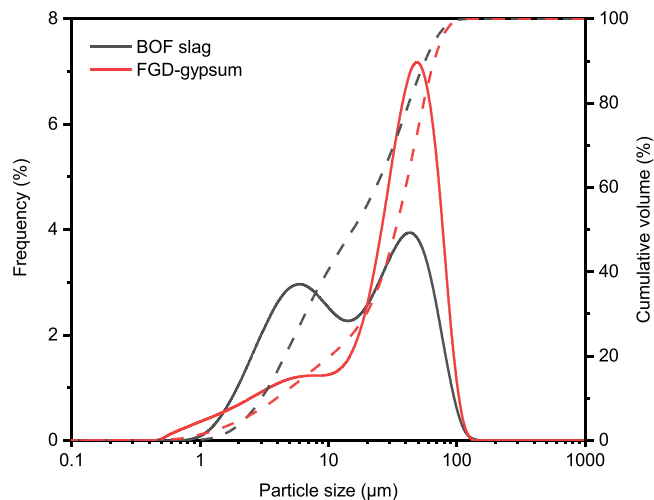
Fig. 1. Chemical structure of DTPA–5Na (C₁₄H₂₃N₃Na₅O₁₀).

Table 1

Chemical composition of BOF slag and FGD gypsum (wt%).

Oxides	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	CaO	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	MnO	Fe ₂ O ₃	Br	LOI
BOF	7.8	2.0	14.2	1.6	-	40.5	1.4	1.0	0.3	4.7	26.9	-	-0.6*
FGD	-	1.0	0.5	-	45.6	28.9	-	-	-	-	0.1	2.6	21.3

*: The oxidation of metallic or divalent iron induces a mass increase during the LOI test.

**Fig. 2.** XRD patterns of the raw BOF slag and FGD gypsum. (b- brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$, c- alpha' and beta dicalcium silicate Ca_2SiO_4 , g- gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, m- magnetite Fe_3O_4 , o- bayerite $\text{Al}(\text{OH})_3$, q- quartz SiO_2 , w- wüstite, FeO .)**Fig. 3.** Particle size distribution of BOF slag and FGD gypsum.

2.2. Specimen preparation

The mixes were designed in two sets (Table 2). The pure BOF slag was activated with 0, 0.5, and 1.0 wt% DTPA-5Na (relative to BOF slag). Although higher dosages of DTPA-5Na can enhance the hydration of BOF slag, their use should be minimized to maintain cost-effectiveness, thereby not included in this study. Secondly, to reveal the impact of the FGD gypsum on the performance of BOF slag binder, 0.5, 1.5, 2.5, 3.5 wt% FGD gypsum (relative to BOF slag) was added in the 1.0 wt% DTPA-5Na-activated BOF slag system. The samples are named with the percentage of DTPA-5Na and FGD gypsum, e.g., D1.0F1.5 represents 1.0 wt% DTPA-5Na and 1.5 wt% FGD gypsum.

According to a preliminary study [6], all pastes were prepared with a water-to-solid (w/s) ratio of 0.18 to achieve sufficient workability. The activator solution was prepared by dissolving the required DTPA-5Na in deionized water one day prior to paste preparation. All pastes were prepared according to EN196-1, casting in styrofoam moulds with a size of $40 \times 40 \times 160 \text{ mm}^3$. The samples were then sealed with layers of cling film to prevent moisture loss and carbonation and cured at $20 \pm 1^\circ\text{C}$ and RH of 60% until the testing ages.

2.3. Methodology

2.3.1. Hydration kinetics and reaction process at an early age

The hydration kinetics of BOF slag-based binder was investigated using an isothermal calorimeter (TAM Air, Thermometric) maintained at a constant temperature of 20°C . Paste samples, as listed in Table 2, were prepared, injected into sealed glass ampoules and promptly placed within the calorimeter channels. The initial peak occurring within the first 30 min, attributed to the dissolution of raw materials, was excluded from the analysis. Measurements of heat flow and cumulative heat were recorded over 7 d after sample mixing. The heat flow and cumulative heat were normalized by the mass of the solid.

To study the early reaction progress of BOF slag-based binder, the evolution of mineralogical compositions was analysed through X-ray diffraction (XRD) analysis. Specifically, samples D0F0 and D1.0F0 were selected to examine the effect of DTPA-5Na on the early hydration process of BOF slag at various curing ages: 0 min, 15 min, 1 h, 3 h, 8 h, 15 h, 24 h and 48 h. Additionally, samples D1.0F0.5 and D1.0F2.5 were chosen to study the effect of FGD gypsum on the early hydration process of DTPA-5Na-activated BOF slag at curing ages of 0 min, 15 min, 45 min, 2 h, 4 h, 6 h, 8 h, 15 h. These curing ages were designated based on the hydration behaviour of each paste. Before the XRD analysis, the hydration of the investigated samples was terminated at the designated curing ages. The samples were crushed into fractions smaller than 1 mm, immersed in isopropanol for 24 h, and subsequently flushed with diethyl ether for 30 min. The samples were then vacuum dried at 40°C for 30 min. The dried samples were ground to pass through a $80 \mu\text{m}$ for XRD analysis. XRD analysis was performed on a Bruker D2 PHASER using $\text{Co K}\alpha$ radiation (30 kV, 10 mA) with a scanning rate of $0.02^\circ (2\theta)$ per step from 10° to $60^\circ (2\theta)$. The XRD patterns were analysed using High-score plus software.

2.3.2. Mechanical properties and microstructural analysis

The initial and final setting time were analysed using a Vicat apparatus. The workability of the fresh BOF slag paste was determined using the mini spread flow table test according to EN 1015-3:2007.

The compressive strength of the paste specimens was assessed after 7 d and 28 d of hydration, following the protocol outlined in EN196-1, with a loading rate of 2400 N/s. Six duplicates for each mixture were used to determine compressive strength.

To elucidate the mechanism of strength enhancement in BOF slag-based binder via DTPA-5Na and FGD gypsum, a series of microstructural analyses were conducted. These included quantitative X-ray diffraction (Q-XRD) analysis, thermogravimetric analysis (TGA), mercury intrusion porosimetry (MIP), and scanning electron microscope (SEM).

Q-XRD analysis was performed on both raw materials and hydrated samples using the Rietveld method [35]. The testing samples were mixed with 10 wt% Silicon Powder (used as an Internal standard) and

Table 2

The designed mixtures and fresh properties of BOF slag-based binders.

Group	BOF slag [g]	DTPA–5Na [g]	FGD [g]	w/s	Flowability [mm]	Initial setting [min]	Final setting [min]
D0F0	100	0	0	0.18	135	25	45
D0.5F0	100	0.5	0		200	60	90
D1.0F0	100	1.0	0		243	80	105
D1.0F0.5	100	1.0	0.5		230	85	110
D1.0F1.5	100	1.0	1.5		220	95	125
D1.0F2.5	100	1.0	2.5		215	110	145
D1.0F3.5	100	1.0	3.5		213	135	175
D1.0S1.5	100	1.0	1.24*		223	85	115

Note: * sodium sulphate (Na_2SO_4) with an equivalent sulphate content to FGD gypsum in D1.0F1.5 was used, and the bound water in FGD gypsum was equivalently replaced by 0.32 g of free water.

milled for 5 min in an XRD-Mill McCrone. The Q-XRD tests were conducted with a step size of 0.02° over a 2θ range from 5° to 90° . The resulting XRD patterns were analysed using High-score plus and quantified using TOPAS Academic software v5.0 [36]. The crystal structural data used for quantitative analysis are detailed in Table 3.

Thermogravimetric analysis was conducted on 28 d samples using a Jupiter STA 449 F1 instrument from Netzsch. Approximately 50 mg of dried powder was used for each test, which was performed at a heating rate of 10 K/min from 40°C to 1000°C under a N_2 environment.

For MIP analysis, 28 d paste samples were crushed into granular pieces approximately 4 mm in size. The total porosity and pore volume distribution of these granular pieces were analysed using a mercury porosimeter (AutoPore IV 9500, Micromeritics). The analysis was conducted over an absolute pressure range from 0.7 kPa to 230 MPa, with a contact angle of 130° .

Powder samples obtained from the crushed 28 d samples were also prepared for SEM and EDS analysis (Phenom Pro). The samples were initially spread on carbon conductive adhesive tape and then coated with gold (Au) for 30 s using a Quorum 150TS plus sputter coater at 30 mA. The morphology of the reaction products was observed in secondary electron mode at a magnification of 15000. Spot EDS analysis was performed at a voltage of 15 kV to characterize the chemical composition of reaction products.

2.3.3. Leaching behaviour of heavy metals

One batch leaching test was conducted on both the raw materials and cured paste samples according to EN12457–2. The cured samples were first crushed to a size smaller than 4 mm and then mixed with deionized water in polyethylene bottles at a liquid-to-solid (L/S) ratio of 10. These bottles were sealed and horizontally placed on a linear reciprocating shaking device (Stuart SSL2) for 24 h, with a constant shaking rate of 250 rpm. Afterwards, the liquids were filtered through a $0.2\ \mu\text{m}$ poly-ether sulfone membrane and acidified with nitric acid to prevent

potential precipitation. The resulting leachate was analysed using an inductively coupled plasma optical emission spectrometer (ICP-OES Spectral Blue) according to NEN 6966.

2.3.4. Hydration model of BOF slag based on Powers and Brownyard Theory

The BOF slag hydration model developed in this study is based on the fundamental framework of the cement hydration model. The pioneering work by Powers and Brownyard accounted for unreacted cement, free water, the hydration products and the chemical shrinkage in their proposed cement paste model [39]. The hydration of individual reactive components was quantified, and their contributions to volume changes were integrated to assess overall chemical shrinkage. Similarly, the BOF slag hydration model was adapted by focusing on the hydration of belite and iron-rich brownmillerite, based on the present findings on its hydration kinetics, with further modifications to reflect the specific phase assemblage of the BOF slag system. Specifically, the water demand calculations are derived from the stoichiometry of the hydration products identified through Q-XRD and TGA in this study, including ettringite, monocarboaluminate, hydrocalumite, portlandite, and C-S-H gel, rather than assuming OPC-specific hydration stoichiometry. The theoretical water demand and chemical shrinkage were then calculated using a refined cement hydration model [40]. Detailed information is provided in Section 3.5.

3. Results

3.1. Hydration kinetics and its correlation with hydration products

The 7 d hydration heat release of BOF slag with water and DTPA–5Na (0.5 wt% and 1.0 wt%) were monitored via isothermal calorimetry to understand the effect of the DTPA–5Na concentration on the early hydration kinetics of BOF slag, as shown in Fig. 4. For D0F0,

Table 3

Structural data of the phases used for the quantitative XRD analysis.

Mineral name	Cement notation	Chemical formula	ICSD	Space group
Silicon	-	Si	43610	Fd-3m
Fe-rich wüstite	RO	$\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}$	67199	Fm-3m
Mg-rich wüstite	RO	$\text{Fe}_{0.3}\text{Mg}_{0.7}\text{O}$	67200	Fm-3m
Magnetite	Ff	Fe_3O_4	30860	Fd-3mZ
Brownmillerite	$\text{C}_2(\text{A}, \text{F})$	$\text{Ca}_2\text{Al}_{0.79}\text{Ti}_{0.61}\text{Fe}_{1.59}\text{O}_5^*$	9197	Pnma
Larnite	$\beta\text{C}_2\text{S}$	Ca_2SiO_4	81096	P121/n1
Alpha'-belite	$\alpha'\text{C}_2\text{S}$	Ca_2SiO_4	81097	Pnma
Lime	-	CaO	28905	Fm-3m
Portlandite	CH	$\text{Ca}(\text{OH})_2$	64950	P-3m1
Calcite	Cc	CaCO_3	80869	R-3c
Quartz	-	SiO_2	90145	P3221
Monocarboaluminate	AFm	$\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3 \cdot 11\text{H}_2\text{O}$	10316	P1
Hydrocalumite	AFm	$\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{Cl}, \text{CO}_3, \text{OH})_{2-4}\text{H}_2\text{O}$	14832	P21
Ettringite	AFt	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$	16045	P31c

*: The chemical formula used for brownmillerite was derived from the chemical composition determined through large area phase mapping analysis conducted on BOF slag samples sourced from the Tata Steel Plant IJmuiden [37,38].

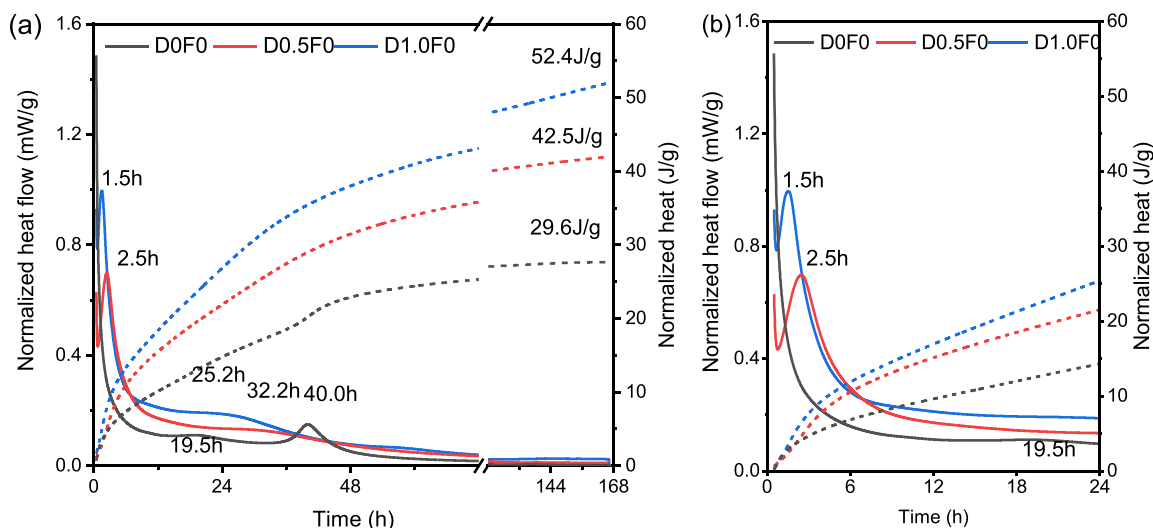


Fig. 4. Cumulative heat and heat flow during the initial (a) 168 h and (b) 24 h of hydration: 0, 0.5 and 1.0 wt% DTPA-5Na-activated BOF slag binder.

the heat flow decreases continuously for the first 15 h, followed by a broad peak with low intensity around 19.5 h, indicating the low reactivity of BOF slag at the early age. After that, a second peak of relatively high intensity occurs around 40.0 h. In order to correlate the dominant reaction process for each exothermic peak, the phase evolution of BOF slag hydrated with water after 15 min, 1 h, 3 h, 8 h, 15 h, 24 h, and 48 h was characterized by XRD analysis, and the results are illustrated in Fig. 5. During this period, the (0 2 0) peak associated with brownmillerite ($2\theta = 13.94^\circ$, $d = 7.30 \text{ \AA}$) gradually diminishes, suggesting its dissolution. Conversely, the (0 0 2) peak of monocarboaluminate ($2\theta = 13.60^\circ$, $d = 7.80 \text{ \AA}$) increases significantly after 8 h hydration. This observation suggests that the early reaction produces monocarboaluminate, predominantly contributing to the exothermic peak observed in D0F0 around 19.5 h. Similar formations have been reported in previous studies, which attributed them to the reactions of aluminate (C_3A and C_{12}A_7) and CaCO_3 [23]. However, the BOF slag used in this study has relatively low aluminium content (see Table 1). Therefore, some of Al (III) is likely to be substituted by Fe (III) in the monocarboaluminate [41]. Determining the specific composition of the reaction products is challenging since these minerals are layered double hydroxides, and the exchange of interlayer metal ions, particularly iron and aluminium, is highly probable. Hereinafter, we refer to it as monocarboaluminate. Subsequently, the (0 0 2) peak ascribed to hydrocalumite ($2\theta = 13.05^\circ$, $d = 7.86 \text{ \AA}$) emerges after 15 h hydration, corresponding to the second exothermic peak. It is worth noting that the formation of C-S-H gel resulting from the hydration of C_2S also generates heat. However, this heat release is believed to be comparatively lower due to the limited extent of early hydration of C_2S [42]. Meanwhile, it should be noted that the dissolution of inherent minerals and the formation of hydration products occur dynamically and may overlap; thus, the heat peaks cannot be attributed to a single reaction but reflects the dominant process.

The incorporation of DTPA-5Na alters the early-age heat release behaviour. An intense peak appears within the first few hours, followed by a broader peak with lower intensity. For 0.5 wt% DTPA-5Na, the peaks occur at 2.5 h and 32.2 h, while for 1.0 wt% DTPA-5Na they shift to 1.5 h and 25.2 h. It should be noted that the phase composition of D1.0F0 in Fig. 5 (c) does not exhibit significant change after 1 h and 3 h of hydration. Therefore, the initial intense peak observed around 1.5 h in the calorimetry test is mainly attributed to the dissolution of brownmillerite, facilitated by the chelating effect of DTPA-5Na. A minor contribution from monocarboaluminate formation is also indicated by small peaks observed in Fig. 5 (d). The primary hydration product in DTPA-5Na-activated BOF slag is monocarboaluminate,

while the formation of hydrocalumite is limited. This limitation is potentially due to the competition for calcium and aluminium. Additionally, there is a demonstrable promotion in the total heat released during the first 168 h of hydration with the introduction of DTPA-5Na, from 29.6 J/g for D0F0 to 42.5 J/g with 0.5 wt% DTPA-5Na, and further to 52.4 J/g with 1.0 wt% DTPA-5Na. This underscores the pronounced acceleration of BOF slag hydration facilitated by DTPA-5Na, with the acceleration extent intricately contingent upon the dosage of DTPA-5Na.

The 7 d hydration heat release of BOF slag activated with 1.0 wt% DTPA-5Na and varying FGD gypsum contents is depicted in Fig. 6. It is evident that the hydration peaks of the binder are significantly delayed with increasing dosage of the FGD gypsum. For example, with 0.5 wt% FGD gypsum, the peak times shift from 1.5 h and 24.2 h to 4.3 h and 45.8 h, respectively. At higher gypsum content (≥ 1.5 wt%), the heat evolution exhibits distinct patterns compared with D0F0 and D1.0F0.5. An initial low-intensity peak appears at 3.3 h, followed by subsequent peaks at 8.4 h, 14.0 h, and 24.2 h, for 1.5, 2.5, and 3.5 wt% FGD gypsum, respectively. To elucidate the underlying reasons for these differing isothermal calorimetry patterns, the phase evolution of D1.0F0.5 and D1.0F2.5 was analysed in Fig. 7.

In the XRD patterns of D1.0F0.5, the peak corresponding to incorporated FGD gypsum ($2\theta = 13.45^\circ$, $d = 7.61 \text{ \AA}$) decreases continuously and disappears after 2 h, indicating rapid dissolution during early hydration process. Subsequently, distinct peaks of monocarboaluminate emerge after 4 h, identified as the primary contributor to the exothermic peak around 4.3 h in Fig. 6 for D1.0F0.5. Remarkably, the entire exothermic peak in D1.0F0.5 can be attributed to the combined effects of FGD gypsum dissolution and monocarboaluminate generation, as well as the dissolution of brownmillerite. In the case of D1.0F2.5, gypsum is completely consumed after 6 h, consistent with the anticipated prolonged dissolution duration for a higher gypsum dosage. Consequently, the initial exothermic peak around 3.3 h in Fig. 6 for D1.0F2.5 is associated with the dissolution of FGD gypsum. The subsequent exothermic peak around 14.0 h primarily corresponds to the monocarboaluminate formation, supported by the emergence of its distinctive peaks after 15 h. This finding also indicates that the addition of FGD gypsum retards the dissolution of brownmillerite. The rapid increase in Ca^{2+} concentration from gypsum dissolution would effectively compete with Ca^{2+} released from BOF slag phases for the available DTPA-5Na, given the limited chelator dosage (≤ 1.0 wt%) in this system. This competition reduces the effective concentration of free DTPA available for chelating Ca^{2+} from slag dissolution, thereby temporarily moderating the chelation-promoted dissolution of reactive slag phases and shifting the

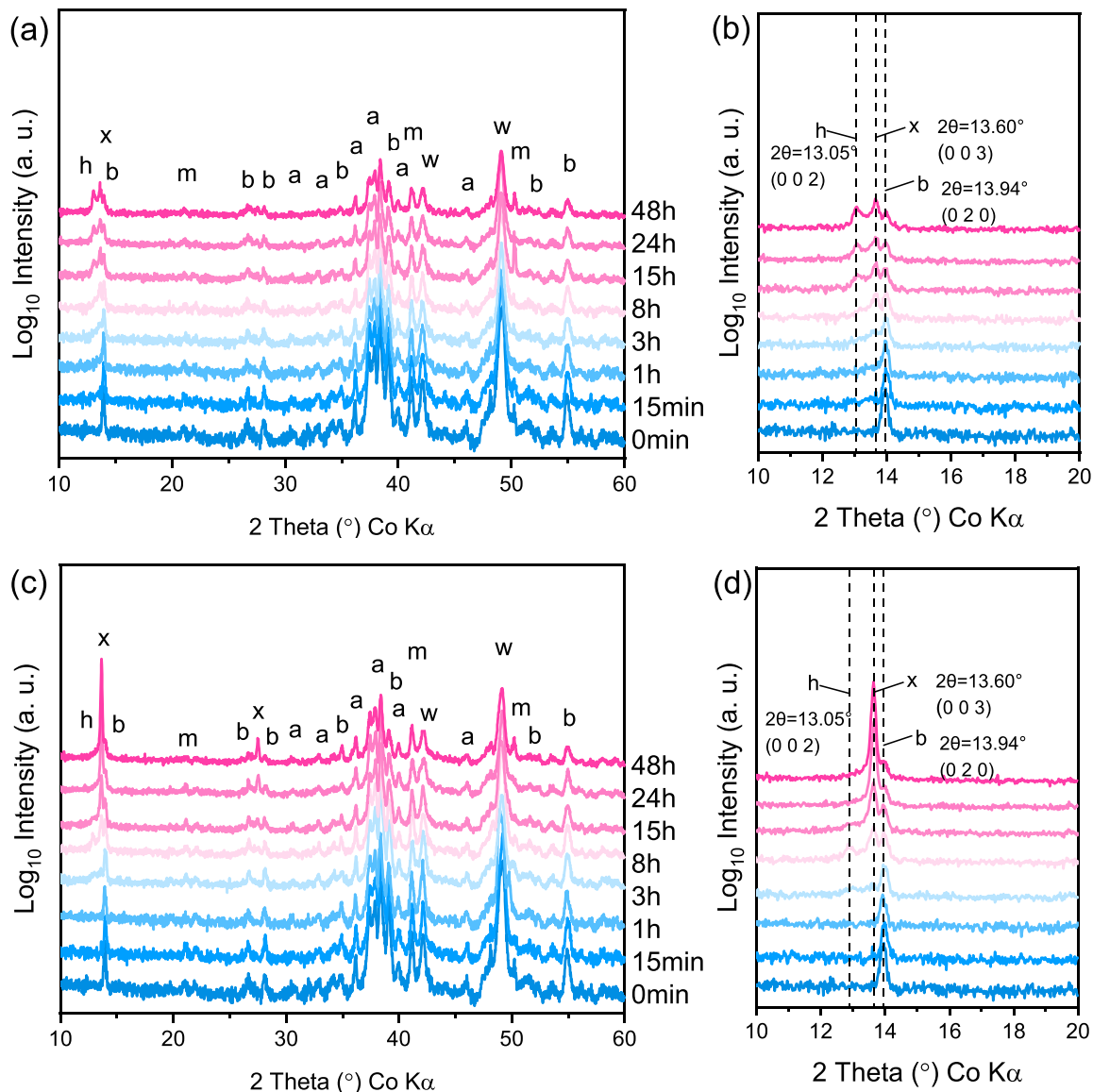


Fig. 5. Phases evolution of D0F0 (a-b) and D1.0F0 (c-d) after 0 min, 15 min, 1, 3, 8, 15, 24 and 48 h. (a, c) 2θ ranges from 10° to 60° , and (b, d) 2θ ranges from 10° to 20° . The patterns are displaced vertically for clarity. (a- α' and β dicalcium silicate, b- brownmillerite, m- magnetite, p- portlandite w- wüstite, h- hydrocalumite, x- monocarboaluminate).

hydration peaks to later ages. Additionally, a small peak at $2\theta = 10.47^\circ$, indicative of ettringite, is discernible after 8 h hydration in the XRD patterns of D1.0F2.5. Its low intensity reflects the scarce formation at early age yet confirms the influence of gypsum on hydration products. In summary, both DTPA-5Na and FGD gypsum significantly influence the hydration process of BOF slag binder and the associated hydration products, thereby providing opportunities to tailor the overall properties of this binder.

3.2. Effects of DTPA-5Na and FGD gypsum on mechanical properties

The compressive strength development for each paste is illustrated in Fig. 8. As anticipated, the paste containing only water exhibits relatively low compressive strength at 7 and 28 d, measuring around 4.8 and 9.4 MPa, respectively, due to the limited hydration degree of BOF slag. In comparison, a notable increase in compressive strength is observed with the addition of DTPA-5Na as an activator. For instance, at 28 d, D1.0F0 attains 22.5 MPa, indicating a significant enhancement in the hydration degree of the BOF slag. Further enhancement is observed with

the incorporation of FGD gypsum, with D1.0F3.5 achieving a compressive strength of 35.8 MPa at 28 d. This significantly improved compressive strength highlights the synergistic effect of DTPA-5Na activation and FGD gypsum incorporation on BOF slag hydration, demonstrating its great potential as a supplement to Portland cement binder.

3.3. Enhancement mechanism of DTPA-5Na and FGD gypsum

3.3.1. Q-XRD analysis

To figure out the enhancement mechanism of DTPA-5Na and FGD gypsum on BOF slag hydration, their effects on the phase composition were evaluated through the Q-XRD analysis, with the results summarized in Fig. 9 and Table 4. When the BOF slag is hydrated with water in Fig. 9 (a), only traces of hydrocalumite and monocarboaluminate are detected, consistent with the early-stage phase evolution observed in Fig. 5. Notably, the hydrocalumite peak shifts from $2\theta = 13.05^\circ$ (Figs. 5) to 12.95° (Fig. 9 (a)). This shift in layered double hydroxides suggests an expansion in the interlayer spacing, likely due to the substitution of

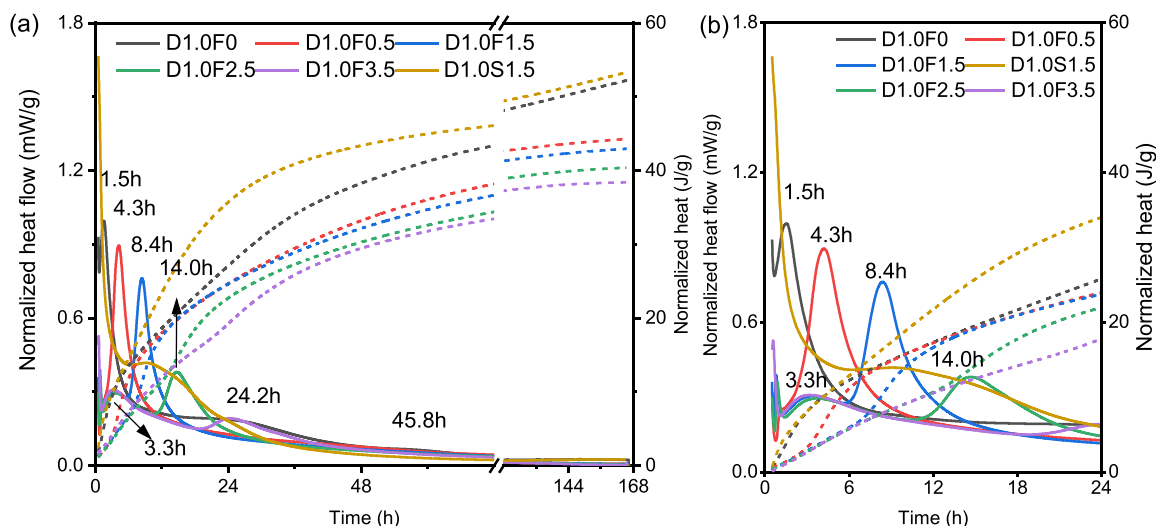


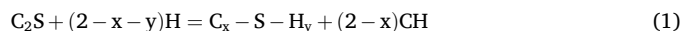
Fig. 6. Cumulative heat and heat flow during the initial (a) 168 h and (b) 24 h of hydration: 1.0 wt% DTPA–5Na-activated BOF slag binder with varying dosages of FGD gypsum (0–3.5 wt%).

hydroxides with carbonate ions with ages [43]. Meanwhile, brownmillerite and amorphous contents decrease to 12.7 wt% and 13.5 wt%, respectively, suggesting that, without activation, reactivity of BOF slag primarily resides in brownmillerite and C_2S . Upon activation of DTPA–5Na, the intensity of monocarboaluminate peak increases significantly, accompanied by a marked reduction in brownmillerite as confirmed in Table 4. Additionally, the hydrocalumite peak becomes undetectable, indicating that DTPA–5Na facilitates monocarboaluminate formation while hindering hydrocalumite production, likely due to the preferential consumption of calcium and aluminium. The incorporation of FGD gypsum leads to the emergence of the peak associated with hydrocalumite in Fig. 9 (b), with its intensity escalating in proportion to the FGD gypsum dosages. Detailly, the hydrocalumite increases to 2.6–3.1 wt%, while monocarboaluminate decreases to 3.5 wt%. This observation can be explained by FGD gypsum supplying adequate Ca^{2+} ions, thereby facilitating the formation of hydrocalumite. Compared with D0F0, the hydrocalumite formed in FGD gypsum-modified samples shows a specific peak shift to lower angle ($2\theta = 12.77^\circ$). The shift is potentially induced by the incorporation of sulphate ions in the interlayer [44]. Moreover, the addition of FGD gypsum promotes the formation of ettringite, reaching up to 6.3 wt% at 3.5 wt% FGD gypsum. This observation is consistent with the results obtained during the early hydration stage of D1.0F2.5, as illustrated in Fig. 7. More importantly, the residual brownmillerite content decreases progressively from 10.6 wt% in D1.0F0 to 7.7 wt% in D1.0F2.5, suggesting that gypsum facilitates brownmillerite dissolution by promoting ettringite precipitation, which reduces Ca^{2+} and Al^{3+} concentrations in the pore solution and sustains the thermodynamic driving force for dissolution. However, a slight increase is observed in D1.0F3.5 (8.9 wt%), possibly attributable to the formation of a dense ettringite network around unreacted slag particles at higher gypsum dosages, which impedes water access to the brownmillerite surface.

3.3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) were performed on 28 d samples, with the results depicted in Fig. 10. For D0F0, a total mass loss of approximately 4 wt% can be observed over the temperature range, mainly attributed to the release of bound water and CO_2 from hydrates and carbonates. The primary mass loss, occurring notably between 120 °C and 180 °C, is associated with the dehydration of monocarboaluminate [45,46], while minor peaks around 100 °C and 460 °C are attributed to the dehydration

of C–S–H gel and portlandite, respectively [6,47], confirming limited C_2S hydration in the absence of water, as described by [48]:



Additional broad peaks at around 620 °C and 700 °C (P1 and P2) are linked to carbonate decomposition. The presence of carbonates indicates some carbonation occurring during the preparation and curing processes despite careful sealing and vacuum drying of the samples.

The introduction of DTPA–5Na and FGD gypsum in the BOF slag system induces an increased total mass loss, approximately ranging from 6% to 10%, reflecting an enhanced hydration degree of the BOF slag. Detailly, applying DTPA–5Na to the BOF slag results in an increased mass loss attributed to the dehydration of monocarboaluminate and C–S–H gel. Incorporation of FGD gypsum into 1.0 wt% DTPA–5Na activated BOF slag induces a significant additional mass loss around 100–130 °C, ascribed to the dehydration of ettringite, which increases with gypsum dosages, providing further evidence of its correlation with ettringite formation. Therefore, the enhanced mechanical performance resulting from the extra formation of ettringite can be inferred. Meanwhile, portlandite initially increases with 0.5 wt% FGD gypsum but declines with further increases in FGD gypsum content. This trend may be attributed to the extra consumption of Ca^{2+} by the formation of ettringite than portlandite, as the equilibrium formation of C–S–H gel with C_2S dissolution would permit a certain concentration of Ca^{2+} , sufficient for transforming low FGD dosages into ettringite. However, higher FGD dosages consume more Ca^{2+} , consequently inhibiting portlandite formation. This reduction in portlandite parallels findings in the hydration of C_3S with additional gypsum [49]. Unfortunately, identifying the mass loss attributed to the dehydration of C–S–H gel in the FGD-modified BOF slag system poses challenges, as it overlaps with the dehydration of ettringite.

3.3.3. Pore structure

Fig. 11 (a) shows the total porosity and average pore size of BOF slag pastes after 28 d hydration obtained by MIP test. The BOF slag paste hydrated with water (D0F0) has the highest total porosity of 27.1% and an average pore size of 68.0 nm, consistent with its low hydration degree and only irregular particles observed in Fig. 11 (c). The irregular particles show higher silicon concentration due to its limited reactivity (Supplementary Materials Table S2). With 1.0 wt% DTPA–5Na, the total porosity decreases to 23.0%, and the average pore size reduces to 39.1 nm, accompanied by the formation of flaky AFm phase that are

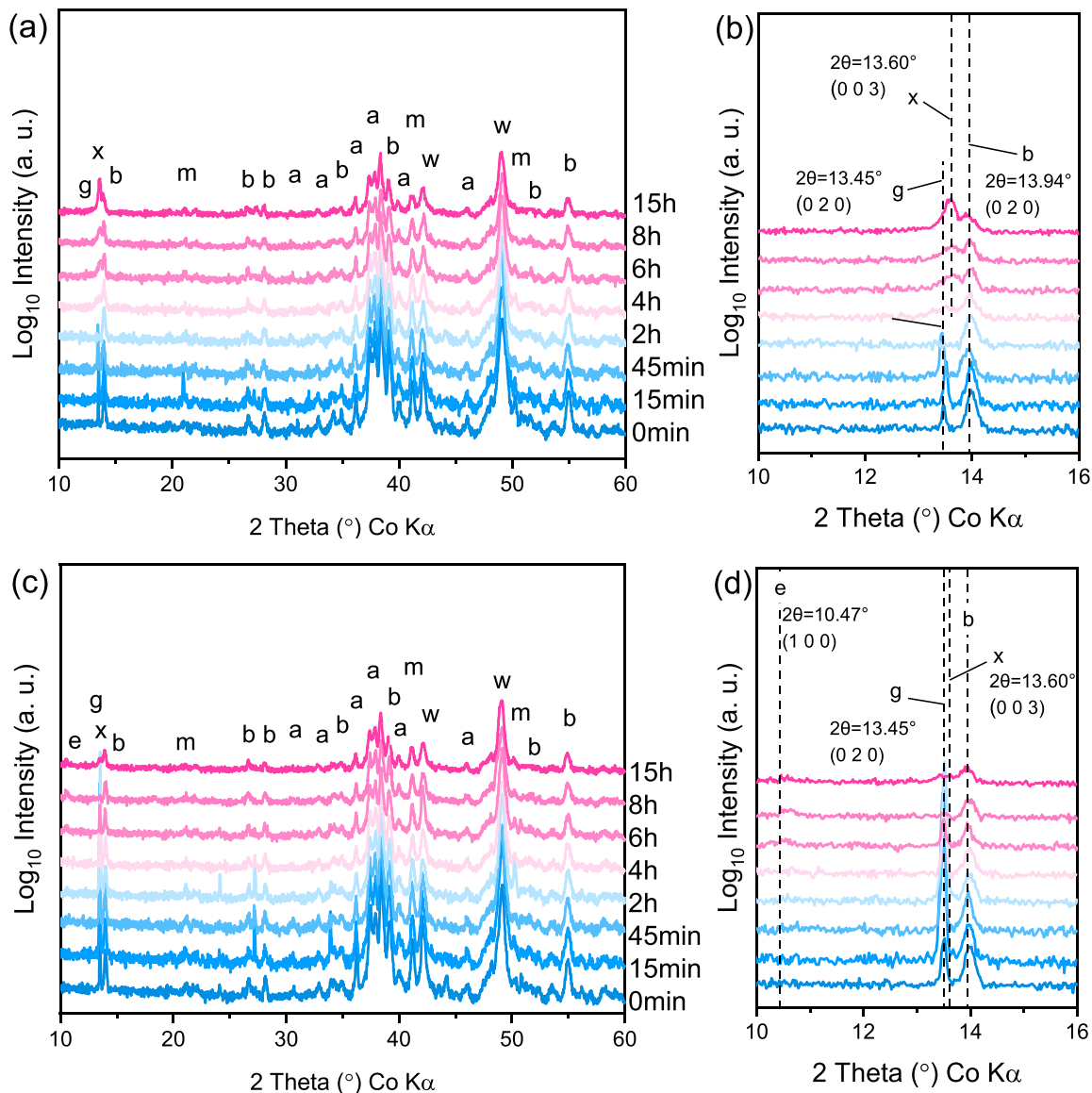


Fig. 7. Phases evolution of D1.0F0.5 and D1.0F2.5 after 0 min, 15 min, 45 min, 2, 4, 6, 8 and 15 h. (a, c) 2θ ranges from 10° to 60° , and (b, d) 2θ ranges from 10° to 16° . The patterns are displaced vertically for clarity. (a- α' and β dicalcium silicate, b- brownmillerite, e- ettringite, g- gypsum, m- magnetite, p- portlandite wüstite, x- monocarboaluminate).

well distributed throughout the matrix. The flaky AFm is further verified by the higher aluminium and calcium concentrations, consistent with composition of the formed monocarboaluminate. Furthermore, upon adding FGD gypsum to the DTPA–5Na-activated BOF slag, additional enhancements are noted. Specifically, with the incorporation of 3.5 wt% FGD gypsum, the total porosity is diminished to 18.7%, and the average porosity is reduced to 23.7 nm. Some rod-like ettringite are well distributed in the matrix, which are also verified by the enhanced aluminium and sulphate concentration in Table S2. The decrease in total porosity aligns with the enhanced mechanical performance depicted in Fig. 8, suggesting a correlation between reduced porosity and improved mechanical properties.

To elucidate the effect of DTPA–5Na and FGD gypsum on the pore structure in detail, the evolution of four types of pores - macro-pore (> 100 nm), capillary pore ($50 - 100$ nm), middle capillary pore ($10 - 50$ nm), and gel and mesopore (< 10 nm) was investigated, based on classification from literature studies [50]. The pore volume distribution of each paste is illustrated in Fig. 11 (b). It is observed that the paste D0F0 exhibits the highest volume of pores > 100 nm, which explains its low strength properties. Upon the activation of DTPA–5Na, pores ($>$

100 nm) become filled with more reaction products, forming additional capillary pores. A similar reduction in the macro-pores volume is noted after the incorporation of FGD gypsum, indicating the filling effect of the formed ettringite. Notably, a significant increase in gel pores and mesopores is observed when 3.5% FGD gypsum is utilized, which suggests a refinement in the pore structure, contributing to improved mechanical properties and overall performance of the paste.

3.4. Environmental impact

Certain heavy metals can persist during steel manufacture in BOF slag, raising concerns about their leaching potential and resulting environmental impacts when utilized as building materials. The leaching behaviour of raw materials and 28 d cured paste samples have been characterized, with findings detailed in Table 5. In raw BOF slag, Chromium (Cr), Molybdenum (Mo) and Vanadium (V) are detected, all below the permissible limit specified by the Dutch soil quality decree.

Upon 28 d hydrated BOF slag with water (D0F0), there is increased leaching of Cobalt (Co), Mo and V. This heightened leaching is attributed to mineral dissolution during the hydration process. Santos et al.

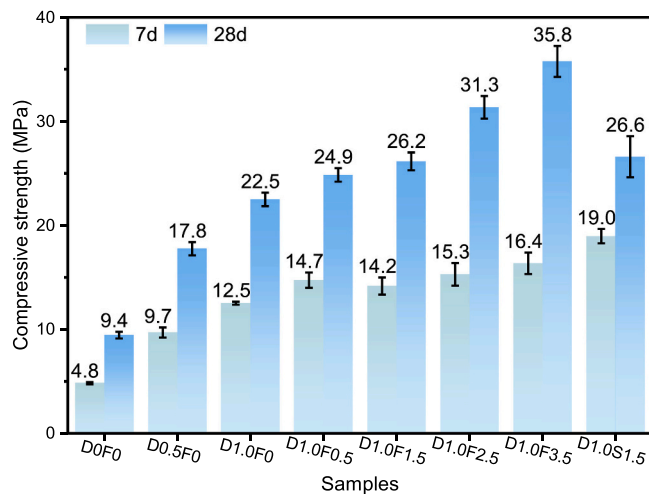


Fig. 8. Effect of DTPA–5Na and FGD gypsum content on compressive strength development.

have revealed the distribution of Cr and V within the BOF slag mineral phases, with Cr mostly incorporated in wüstite and brownmillerite and V predominantly found in C_2S and brownmillerite [51]. Hence, the promoted dissolution of brownmillerite, as indicated by the XRD patterns in Fig. 5, contributes to these increased leaching levels.

Meanwhile, the addition of DTPA–5Na results in increased leaching of most heavy metals due to the promoted mineral dissolution. However, the leaching of V decreases, possibly due to the precipitation of $Ca_3(VO_4)_2$ ($\log K_{sp} = -17.97$) under alkaline conditions ($pH \approx 12$) [52]. The equilibrium formation of C-S-H phases with C_2S dissolution would allow for high Ca^{2+} concentration in the leachate and limit the solubility of $Ca_3(VO_4)_2$ [53]. Hence, more V is solidified and remains embedded within the matrix.

The incorporation of FGD gypsum diminishes Cr leaching. Previous studies have indicated that Cr(VI) is the predominant form in BOF slag leachate, as opposed to Cr(III) [54]. At a pH of around 12, Cr(VI) primarily exists as CrO_4^{2-} . Consequently, the addition of $CaSO_4$ promotes the precipitation of $CaCrO_4$ ($\log K_{sp} = -5.29$). Moreover, it has been reported that the ettringite formed in FGD-modified BOF slag can immobilize CrO_4^{2-} within its molecular structure [55]. Enhanced ettringite formation consequently leads to greater immobilisation of Cr. It should also be mentioned that Cr(III) precipitates as $Cr(OH)_3$ under high pH conditions, further contributing to the reduction of Cr leaching. However, the leaching of V increases as ettringite formation consumes Ca^{2+} , resulting in less $Ca_3(VO_4)_2$ precipitation. In the case of Co, Cu, Mo and Ni, their leaching levels vary with increased FGD gypsum, likely due to altered equilibrium formation of hydrocalumite, ettringite and C-S-H gel, which have different immobilization capacities of heavy metals [56–60]. Overall, the prepared BOF slag pastes exhibit satisfactory levels of heavy metals leaching, thus validating their suitability as environmentally friendly binders.

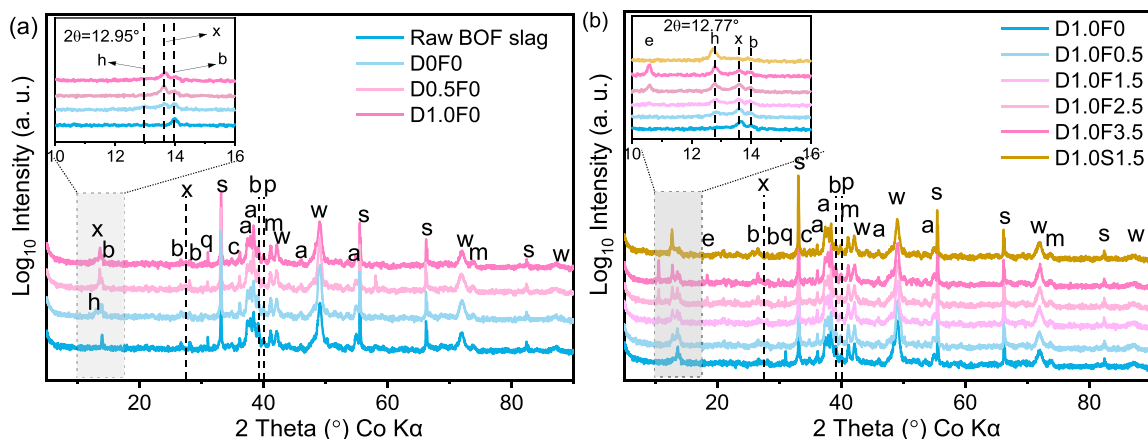


Fig. 9. (a) XRD patterns of the raw BOF slag and 28 d BOF slag (D0F0, D0.5F0 and D1.0F0). (b) XRD patterns of the 28 d BOF slag (D1.0F0, D1.0F0.5, D1.0F1.5, D1.0F2.5, D1.0F3.5 and D1.0S1.5). The patterns are displaced vertically for clarity. (a - α' and β dicalcium silicate, b - brownmillerite, c - calcite, e - ettringite, m - magnetite, p - portlandite, w - wüstite, h - hydrocalumite, q - quartz, x - monocarboaluminate).

Table 4

The phase composition of the hydrated samples normalized to 100 g of anhydrous raw BOF slag [g].

Phase	Raw BOF	D0F0	D0.5F0	D1.0F0	D1.0F0.5	D1.0F1.5	D1.0F2.5	D1.0F3.5
Wüstite	23.1	23.2	22.8	21.8	20.1	22.0	20.4	22.0
Belite *	34.6	32.4	32.1	30.3	28.5	30.4	28.3	24.7
Magnetite	5.7	5.5	5.4	5.5	5.3	5.9	4.9	4.4
Brownmillerite	15.9	12.7	10.5	10.6	8.3	7.9	7.7	8.9
Lime	0.7	-	-	-	-	-	-	-
Calcite	0.8	0.8	0.2	1.5	2.8	0.5	0.4	0.7
Portlandite	0.2	0.3	0.2	0.0	0.3	0.4	0.3	0.6
Monocarboaluminate	-	4.6	7.1	6.0	6.5	4.2	5.3	2.6
Hydrocalumite	-	1.7	0.2	1.4	2.3	2.6	2.5	3.3
Ettringite	-	0.0	0.0	0.0	0.0	1.1	3.6	6.3
Amorphous	18.3	13.5	14.8	16.1	19.6	18.8	18.9	19.0

*: Total of the Larnite and α' -belite. The original data from TOPAS is provided in Supplementary Material Table S1. Note: The raw BOF slag contains 18.3 wt% of amorphous content, largely introduced during the milling process of the raw materials. This amorphous fraction is primarily comprised of the C_2S phase [6].

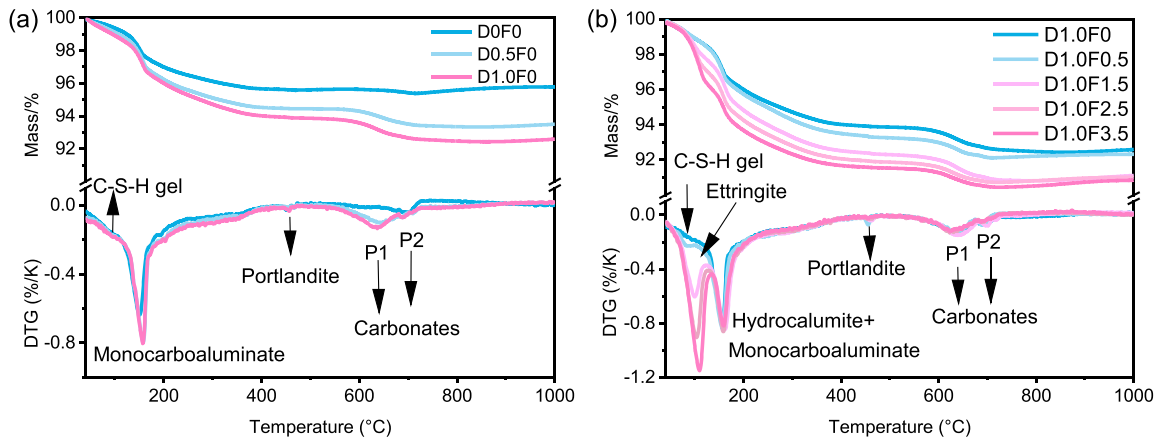


Fig. 10. TG and DTG curves of the 28 d BOF slag (a) 0–1.0 wt% DTPA–5Na (b) 0–3.5 wt% FGD gypsum.

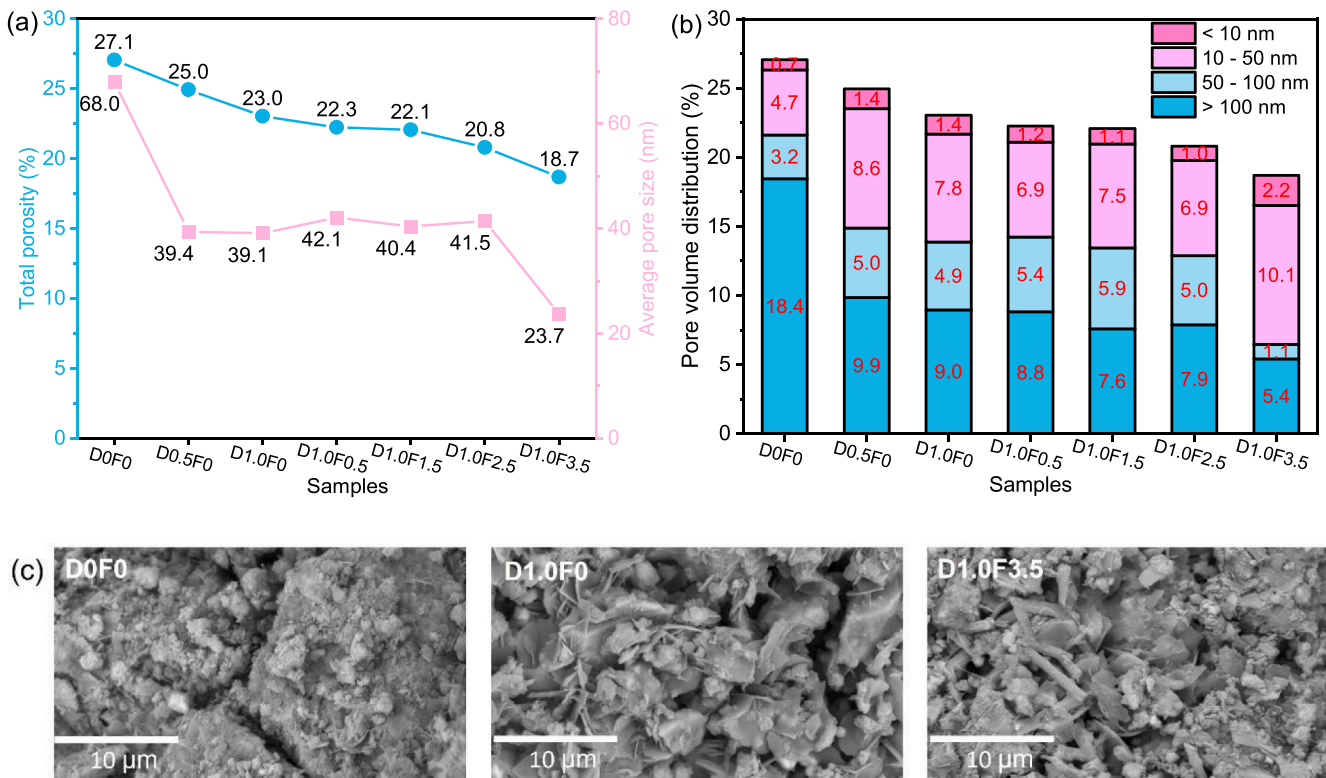


Fig. 11. (a) Total porosity and average pore size, (b) pore volume distribution of 28 d samples, (c) SEM-SE image of the 28 d D0F0, D1.0F0 and D1.0F3.5.

3.5. BOF slag hydration model: theoretical water demand and chemical shrinkage

Based on the Q-XRD and TG analysis, the primary reactive components in BOF slag are C_2S and brownmillerite, leading to the formation of monocarboaluminate, hydrocalumite and C-S-H gel. It is noteworthy that BOF slag contains limited C_3S content, resulting in a hydration process distinctly different from that of Portland cement. Overall, the reactivity of C_2S is low, and early strength development is highly dependent on the hydration of brownmillerite. After the activation of DTPA–5Na, the dissolution of brownmillerite is accelerated, while other minerals such as wüstite and magnetite exhibit limited significant changes. Hence, the hydration of BOF slag post-DTPA–5Na activation can be simplified to the hydration of C_2S and brownmillerite. The

theoretical water demand required for the fully hydration of BOF slag is thereby calculated according to the following reactions [40,61,62]:

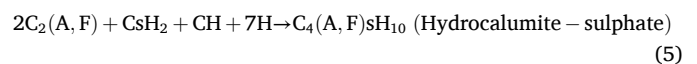
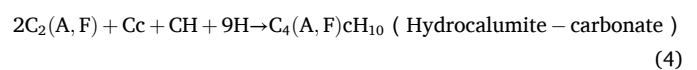
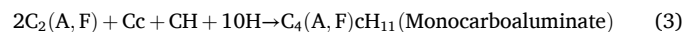
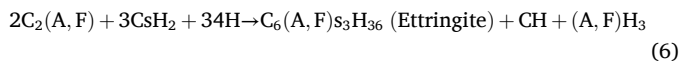


Table 5

The leaching behaviour of the heavy metals from the raw BOF slag, FGD gypsum and 28 d paste samples obtained through one batch leaching test at a liquid to solid of 10, and the SQD legal limit values. All values are in mg/kg dry raw materials. (L.D. - Lower than the detection limits.).

Elements	Co	Cr	Cu	Mo	Ni	V
Raw BOF	L.D.	0.07	L.D.	0.17	L.D.	0.29
Raw FGD	L.D.	L.D.	L.D.	L.D.	L.D.	0.01
D0F0	0.01	0.04	L.D.	0.27	L.D.	0.68
D0.5F0	0.36	0.13	0.13	0.43	0.24	0.63
D1.0F0	0.41	0.14	0.26	0.44	0.25	0.05
D1.0F0.5	0.37	0.03	0.68	0.42	0.21	0.36
D1.0F1.5	0.39	0.02	0.49	0.47	0.22	0.41
D1.0F2.5	0.41	0.02	0.77	0.55	0.21	0.52
D1.0F3.5	0.18	0.01	0.43	0.71	0.17	0.41
Limits	0.54	0.63	0.9	1.0	0.44	1.8



whereby the reaction products (monocarboaluminate and hydrocalumite) are modified based on the findings in the present study, and the potential incorporation of Al in C-S-H gel is not included as the relatively low content of Al in BOF slag. Meanwhile, $\text{C}_{1.7}\text{SH}_{3.2}$ is adopted as the stoichiometry of the formed C-S-H gel, as its precise composition is not directly measurable in this system. Notably, while a lower or higher Ca/Si ratio than assumed would lead to slight overestimation or underestimation of the chemical shrinkage, respectively, the Ca/Si ratio of C-S-H in slag-based systems reported in the literature falls within a relatively narrow range, and the resulting uncertainty in the calculated chemical shrinkage is therefore expected to be limited. Additionally, based on the a previous study on the chemical composition of BOF slag via XRD Rietveld analysis and Phase Recognition and Characterization analysis [6], the amorphous fraction in the raw BOF slag corresponds to XRD-amorphous C_2S produced during the milling process. The density of the amorphous C_2S is assumed equivalent to that of its crystalline counterpart due to the lack of a specific measured value. Considering that only monocarboaluminate or hydrocalumite can form, depending on the regional available water content, the calculated water demand for pure BOF slag, expressed as water/slag mass ratio, is 0.22 ~ 0.23. The calculation process is detailed in [Supplementary Material Text 1](#).

When the gypsum is included, the total formation of ettringite is restricted by its dosage, given that the brownmillerite content is relatively higher than that of gypsum. Therefore, when gypsum completely contributes to the ettringite formation, the calculated water demand for 3.5 wt% gypsum modified BOF slag, expressed as water/slag mass ratio, is 0.25 ~ 0.26. It is also worth noting that sulphate can be absorbed on calcium silicate hydrates and incorporated into various AFm phases

Table 6

Mineralogical composition of BOF slag and phase properties.

Phase	Mass content in BOF slag [wt%]	Density (TOPAS) [g/cm ³]	Molar mass of pure phases [g/mole]	Molar volume [cm ³ /mole]
Wüstite	27.4	4.600	71.85	15.62
Magnetite	3.7	5.119	55.85	10.91
C_2S	24.5	3.307	172.24	52.08
Brownmillerite	14.3	3.810	271.85	71.35
Lime	0.7	3.432	56.08	16.34
Calcite	0.4	2.813	100.09	36.34
Gypsum	-	2.960	172.16	58.16
Amorphous	18.2			
Portlandite		2.211	74.09	33.51
Monocarboaluminate		2.173	568.46	261.60
Hydrocalumite		1.652	289.46	175.22
Ettringite		1.791	1255.11	700.79
C-S-H		2.25 [40]	213.09	94.70

[63], which in practice further reduce the overall water demand. Overall, low water demand is then theoretically confirmed, facilitating the mixture design of the BOF slag-based cementitious materials.

The total chemical shrinkage can be thereby calculated based on the proposed hydration reactions and data presented in [Table 6](#). As the distinction between amorphous content originating from raw BOF slag and that due to the precipitation of C-S-H gel could not be made through Q-XRD analysis in this study, the quantity of C-S-H gel was determined based on the bound water in 28 d hydrated samples (from the thermogravimetric analysis, 4.52 g for D0F0, 6.54 g for D1.0F0 and 9.19 g for D1.0F3.5 per 100 g_{slag}). Specifically, the amount of water bound in hydrocalumite, monocarboaluminate, portlandite and ettringite was calculated, with all remaining water assumed to be incorporated into C-S-H gel. The amount of C-S-H gel was then calculated and subsequently subtracted from the total amorphous content to estimate the content of unreacted XRD-amorphous C_2S . After 28 d hydration, the total chemical shrinkage of D0F0 is 2.0 ml/100 g_{slag}, which translates to 5% volume reduction. This value is substantially lower than that for OPC (6 ~ 9 ml/100 g_{cement}) [64] or GGBFS slag (11 ~ 15 ml/100 g_{slag}) [65]. The low chemical shrinkage is attributed to the low hydration degree of C_2S after 28 d, as well as the high level of inert in the BOF slag. The detailed phase composition of BOF slag (D0F0, D1.0F0 and D1.5F0) hydrated for 28 d is presented in [Fig. 12 \(a\)](#). Upon activation of DTPA-5Na, the chemical shrinkage increases to 3.0 ml/100 g_{slag} due to the enhanced reaction degree of brownmillerite and amorphous C_2S . Integration of gypsum further elevates the chemical shrinkage to 3.5 ml/100 g_{slag}. Interestingly, the addition of gypsum facilitates the hydration of amorphous C_2S and brownmillerite. As a result, a greater amount of free water is bound into the hydration products, aligning with the observed increase in chemical shrinkage.

To verify the proposed hydration reaction, the calculated phase composition of hydrated BOF slag is depicted in [Fig. 12 \(b\)](#). A hydration degree of $\alpha = 0.25$ was employed, based on the reaction degree of the C_2S phase after 28 d in [Fig. 12 \(a\)](#). It must be noted that the various water content required for the formation of monocarboaluminate and hydrocalumite influences the calculation of consumed free water, as indicated in [Eqs. \(3\) and \(4\)](#). However, their preferential formation remains unclear. Hence, the hydration of BOF slag is modelled separately assuming the formation of either monocarboaluminate or hydrocalumite. Comparing the volume of D0F0 (42.9 cm³/100 g_{slag}) in [Fig. 12 \(a\)](#), the range of 43.3–42.8 cm³/100 g_{slag} confirms the desirable outcomes from the hydration model of BOF slag. However, some discrepancies in the volume ratios of hydration products, as calculated according to the proposed hydration reaction, can be observed between D0F0 in [Fig. 12 \(a\)](#) and [Fig. 12 \(b\)](#). Several factors may contribute to these variations. 1) The formation of monocarboaluminate and hydrocalumite could be influenced by the localized w/b ratio, which is likely to be lowered during the hydration process. 2) The bound water content might be overestimated, as the termination of the hydration process by isopropanol and diethyl ether cannot exchange all free water [66].

To validate the effect of DTPA-5Na on the activation of brownmillerite, the proposed hydration reaction of BOF slag was employed, and the chemical shrinkage was calculated at a hydration degree of 0.33 and 0.36 for C_2S in D1.0F0 and D1.0F3.5, respectively (as per [Fig. 12](#)). [Fig. 13 \(a\)](#) presents the theoretical volume of D1.0F0 at various hydration degrees of brownmillerite. Comparing these theoretical results with the measured results of D1.0F0, the hydration degree of brownmillerite ranges from 0.37 to 0.56 (> 0.33), confirming that the DTPA-5Na promotes the hydration of brownmillerite. Similar calculations were conducted with hydrated D1.0F3.5 to validate the impact of FGD gypsum on the hydration of brownmillerite. [Fig. 13 \(b\)](#) presents the theoretical volume of D1.0F3.5 at various hydration degrees of brownmillerite. Combining these theoretical results with the measured results of D1.0F3.5, the hydration degree of brownmillerite ranges from 0.60 to 0.82 (> 0.36), confirming that FGD gypsum also contributes to the hydration of brownmillerite. Overall, establishing such a hydration

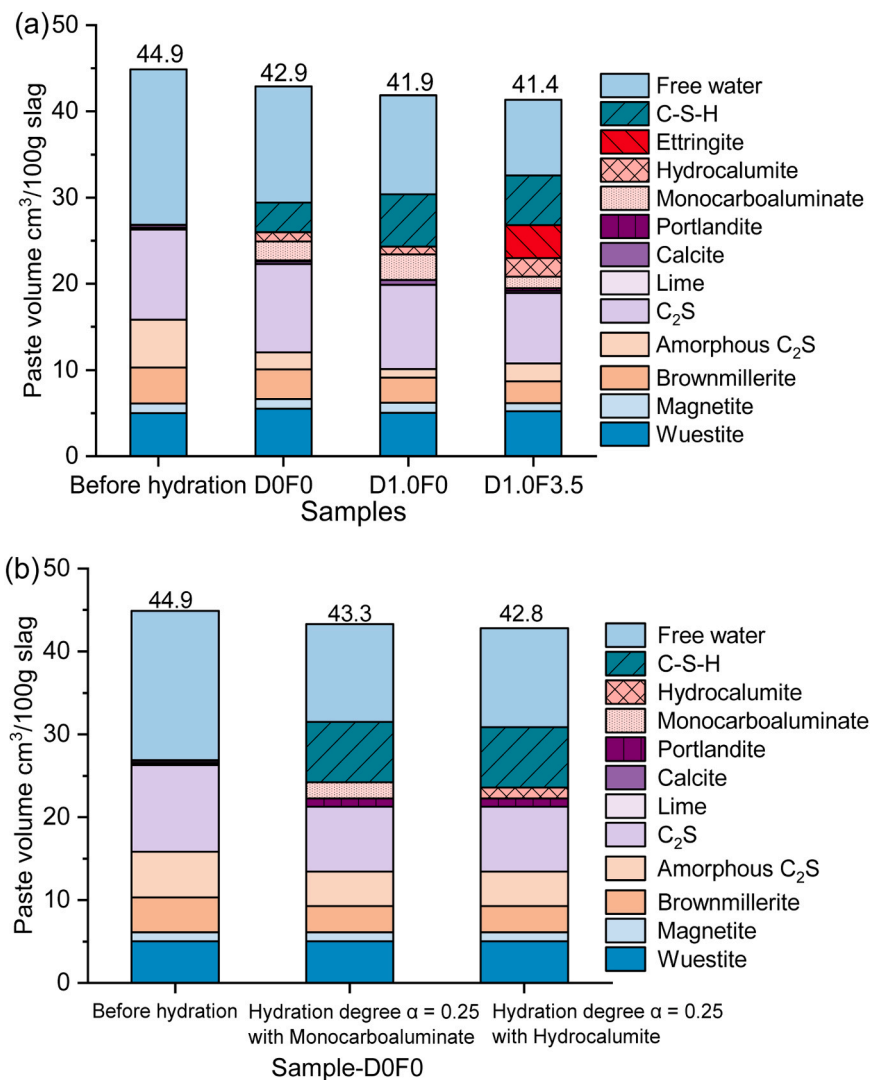


Fig. 12. (a) Composition of BOF slag paste before and 28 d of hydration – D0F0, D1.0F0 and D1.0F3.5 (measured). (b) Composition of BOF slag paste before hydration and D0F0 with only monocarboaluminate or hydrocalumite at the hydration degree of $\alpha = 0.25$ (modelled).

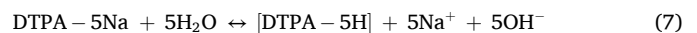
model for BOF slag can help regulate the free-water demand during binder production and enable more reliable estimation of the volume stability of the final materials.

4. Discussion

4.1. New insights in activation mechanism of DTPA–5Na

DTPA–5Na demonstrates its promising potential for activating BOF slag and promoting monocarboaluminate formation. More insight into the chelating reaction between DTPA–5Na and the ions from the BOF slag is provided herein to elucidate the activation mechanism. According to cement hydration theory [67], hydration involves dissolution, saturation, nucleation, and growth, and BOF slag is expected to follow a similar process. The leachable concentrations of key ions ([Ca], [Al], [Fe], [Na]) are determined for both raw materials and DTPA–5Na activated BOF slag (Supplementary Material Figure S2). Raw BOF slag contains a leachable [Al] of 31.63 mg/Kg, [Fe] of 0.04 mg/Kg, [Na] of 14.5 mg/Kg and [Ca] of 4130 mg/Kg. The sufficient [Al] and [Ca] ions support the formation of monocarboaluminate and hydrocalumite. After the 28 d hydration, [Al] and [Ca] concentrations decrease in D0F0 due to their incorporation into hydration products.

0.5 wt% DTPA–5Na increases [Na] concentration, confirming the dissolution of DTPA–5Na, as represented by



The incorporation of 1.0 wt% DTPA–5Na in D1.0F0 results in almost twice the [Na] content, which consists with the doubled amount of DTPA–5Na, indicating desirable test accuracy. It is noteworthy that there is an increase in [Ca], while [Al] shows a slight decrease, and [Fe] content remains extremely low. This observation deviates from the expected chelation stability order ($\text{Fe(III)} > \text{Al(III)} > \text{Ca(II)}$) [68]. Similar findings have been reported for the chelating ability of EDIPA when tested with CaCl_2 , AlCl_3 , and FeCl_3 solutions, respectively [33]. Therefore, this conflicting phenomenon suggests that relying solely on the known chelating abilities of chelators is insufficient to elucidate the mechanisms of their interactions with multiple metal ions within the BOF slag binder system. The effect of pH of the pore solution on the stability of chelates should be taken into consideration, as the hydration of C_2S in BOF slag provides an alkaline environment [42]. Based on the leaching results in Supplementary Material Figure S1, Fe(III) leaching levels are similarly low (~ 0.01 mg/kg) in both the reference and chelator-containing samples. Given the extremely low solubility of Fe(OH)_3 ($K_{\text{sp}} = 4 \times 10^{-38}$ at 25 °C), Fe(III) is expected to precipitate from

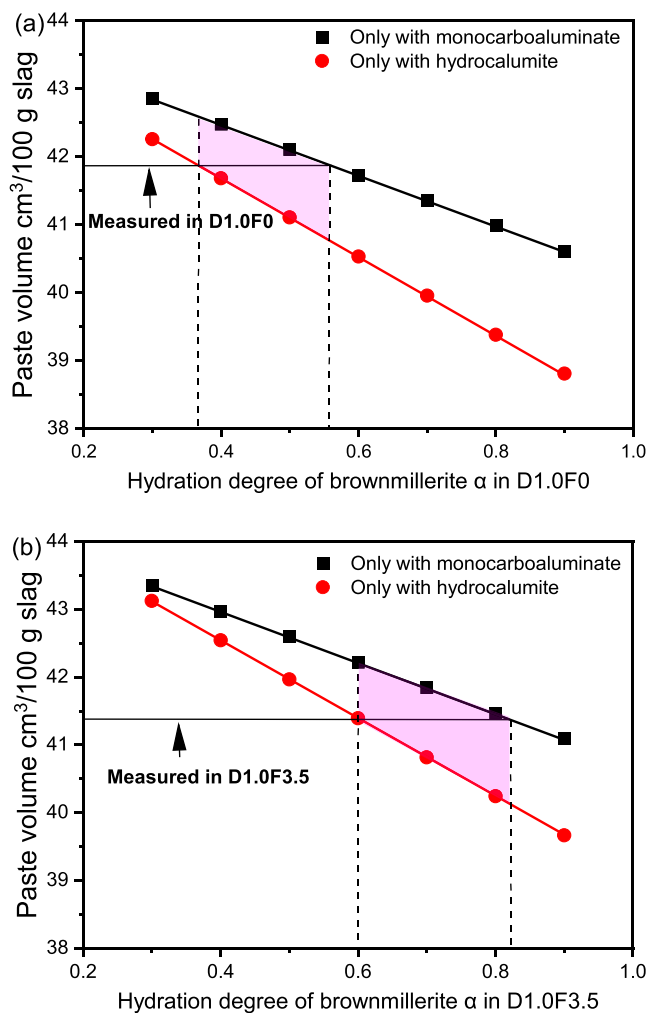
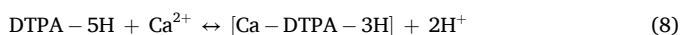


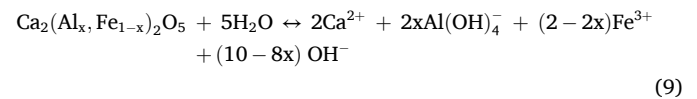
Fig. 13. Theoretical volume of (a) D1.0F0 and (b) D1.0F3.5 at various hydration degrees of brownmillerite (Hydration degree of C_2S was set as 0.33 and 0.36, respectively, according to Fig. 12).

solution under the alkaline conditions of BOF slag hydration, effectively removing it from the pore solution regardless of chelator addition. Consequently, the available DTPA–5Na has limited access to free Fe(III) ions, and Fe(III) immobilization is therefore governed by precipitation rather than chelation. For Al(III), a slight decrease in leaching is observed in the chelator-containing samples (~ 2.5 mg/kg) compared to the reference (~ 6 mg/kg). Al(III) can exist as $\text{Al}(\text{OH})_4^-$ and subsequently be incorporated into hydration products, particularly through the enhanced formation of monocarboaluminate. Most importantly, Ca leaching is slightly higher in the chelator-containing samples (~ 4000 mg/kg) compared to the reference (~ 3500 mg/kg), providing indirect evidence that Ca–DTPA complex formation does occur, resulting in increased Ca^{2+} mobility in the pore solution. Taking together, these leaching results consistently support Ca^{2+} chelation as the dominant complexation pathway of DTPA–5Na under the experimental conditions of this study, as expressed by



Chelated metal ions do not participate in the dissolution balance [23]. Fe(III) and Al(III) may undergo complexation during the initial dissolution stage, but they are subsequently captured within hydration products. Importantly, chelation is equivalent to reducing chelated ions concentration in the aqueous phase. According to Le Chatelier's principle, this promotes forward dissolution progress until a new value of the

dissolution equilibrium constant K is reached [69]. Consequently, the dissolution of brownmillerite is promoted, as per



Overall, the activation mechanism of DTPA–5Na is summarized in Fig. 14, which contributes to an enhanced dissolution and hydration of BOF slag.

4.2. Role of calcium and sulphate on the enhanced mechanism

As observed in Fig. 7, monocarboaluminate forms only after the dissolution of FGD gypsum, indicating that its retardation effect on the hydration of BOF slag is governed by dissolution equilibrium. Taking into account the DTPA–5Na activation mechanism outlined in Section 4.1, more aqueous $[\text{Ca}]$ is chelated, thereby promoting the dissolution of brownmillerite. Therefore, the $[\text{Ca}]$ released from the FGD gypsum also participates in chelation, influencing the overall hydration process also Fig. 14.

To further distinguish the role of $[\text{Ca}]$ and sulphate, sodium sulphate with an equivalent sulphate content (D1.0S1.5) is compared with D1.0F1.5 in terms of the hydration kinetics, mechanical performance and hydration products. As shown in Fig. 6 (b), D1.0S1.5 exhibits a sharp initial heat flow and a main peak at 8.5 h, whereas D1.0F1.5 displays an early minor peak at 3.3 h followed by a major peak at 8.4 h. This discrepancy arises from their contrasting dissolution behaviour: sodium sulphate dissolves rapidly, leading to higher early heat release, while FGD gypsum dissolves more slowly ($K_{\text{sp}} = 2.4 \times 10^{-5}$). Consequently, D1.0S1.5 shows higher cumulative heat the within initial 168 h, indicating a greater overall degree of hydration, which may also account for its higher 7 d compressive strength (19.0 MPa) compared to D1.0F1.5 (Fig. 8). From a phase assemblage perspective (Supplementary Materials Figure S3), D1.0S1.5 forms hydrocalumite rather than ettringite, in contrast to D1.0F1.5. This difference can be attributed to two factors: first, the rapid sulphate release from sodium sulphate favours the formation of hydrocalumite–sulphate according to Eq. (5); second, the absence of additional Ca^{2+} from gypsum dissolution in the sodium sulphate system limits Ca^{2+} availability, which is insufficient to support ettringite formation. At 28 d, D1.0S1.5 and D1.0F1.5 achieve comparable compressive strengths (Fig. 8). Phase analysis (Fig. 9 (b)) shows that D1.0S1.5 primarily forms hydrocalumite with minimal ettringite, whereas D1.0F1.5 forms ettringite, hydrocalumite and monocarboaluminate. This convergence in strength despite differences in phase assemblage suggests that the overall reaction extent, rather than the specific sulphate-bearing phases formed, governs strength development at later stage.

In summary, under DTPA–5Na activation, sulphate addition effectively enhances hydration, while $[\text{Ca}]$ release regulates early-stage hydration kinetics. This suggests that sulphate-rich industrial residues (e.g., phosphogypsum [70], electrolytic manganese residues [71], and gypsum residues generated in copper and zinc-making processes [72,73]) show strong potential as supplementary components in BOF slag-based binders, provided that the effects of associated impurities are adequately controlled. Furthermore, the early strength of these binders can be tailored by selecting sulphate sources with different dissolution rate, offering flexibility for applications such as rapid repairs mortars and specialized concrete formulations.

4.3. Comparison with other chelators and future work

Table 7 summarizes the chelators explored for BOF slag activation, with the primary focus on comparing chelator type, dosage, and resulting strength performance. It should be noted that the water-to-binder ratios, curing conditions, and sample dimensions are not

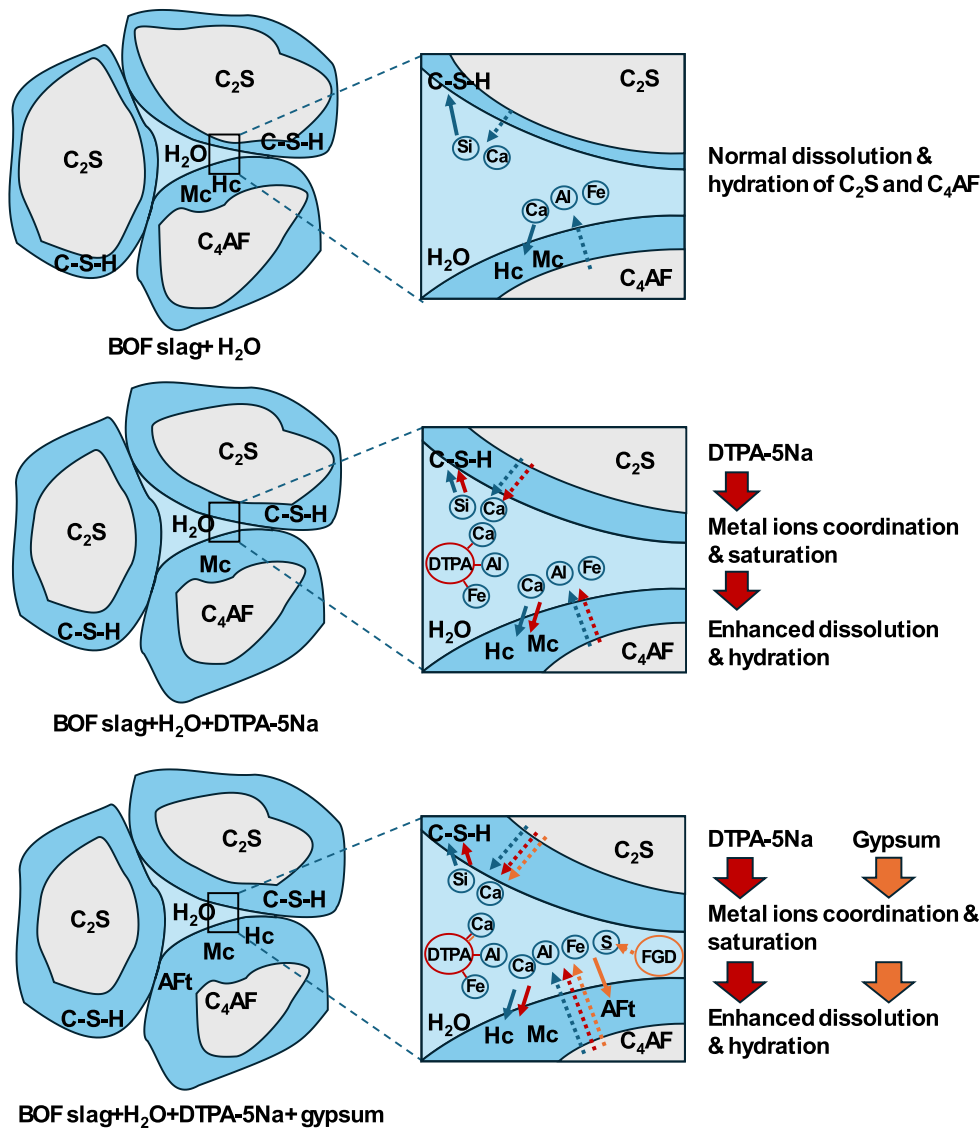


Fig. 14. Schematic diagram of the synergistic activation of DTPA-5Na and FGD gypsum on BOF slag. (Dotted lines indicate dissolution processes, while solid lines indicate precipitation processes. Red lines are associated with DTPA-Na, and yellow lines are associated with FGD gypsum. C₂S-belite, C₄AF-brownmillerite, Mc-monocarboaluminate, Hc-hydrocalumite, Aft-ettringite.).

Table 7
Summary of the chelators activated BOF slag cementitious materials.

Chelators Type	Dosages [wt%]	Slag Fineness d(50) [μm]	w/b	Additives [wt%]	28 d Strength performance [MPa]	Reference
Ethanol-diisopropanolamine (EDIPA)	0–0.1%	13	0.35	35%KOH (0.05 M)	0.96–4.56	[23]
Diethanol- isopropanolamine (DEIPA)	0–0.07%	Not mentioned	0.35	-	0.84–5.74	[74]
Potassium citrate	0–3%	15	0.16	-	20–75	[6]
Tetrasodium ethylenediaminetetraacetate (Na4EDTA)	0–4.8%	10	0.18	-	20–45.1	[21]
Sodium oxalate	0–3%	8.8	0.18	-	19–32.5	[24]
Potassium citrate	0–5%	16	0.18	-	16.2–37.8	[75]
Dipotassium hydrogen phosphate	0–4%	11	0.26	-	20–40	[76]
Dipotassium hydrogen phosphate	0–3%	18	0.18	-	2.5–42.5	[77]
DTPA-5Na	0–1%	18	0.18	-	10–23.5	This study
DTPA-5Na	1.0%	18	0.18	gypsum (0.5–3.5%)	25–37.5	

unified across the compiled studies, and therefore the listed strength values should be interpreted as indicative of the general relation between chelator dosage and mechanical performance rather than as a rigorous quantitative comparison. As shown in Table 7, dosage plays a critical role in determining the mechanical performance of the resulting binder. At low dosages (0.1 wt%) [23,74], chelator addition enhances the hydration of BOF slag but remains insufficient to drive adequate reaction progress, resulting in a relatively low compressive strength below 6 MPa. At higher dosages in the range of 3–5 wt% [6,21,24,75–77], substantially greater strength of 15 ~ 45 MPa are achieved, with value up to 75 MPa reported in [6] under conditions of increased slag fineness and reduced w/b ratio. However, such elevated chelator dosages are primarily required to overcome metal ion saturation by providing sufficient complexation capacity, which raises concerns regarding material cost and potential long-term durability implications. In this study, an alternative strategy is proposed to achieve sufficient mechanical strength at low chelator dosages (<1 wt%) by combining DTPA–5Na with FGD gypsum. This approach simultaneously improves Ca coordination through chelation and reduces Ca saturation through ettringite precipitation, thereby promoting hydration at a significantly reduced activator dosage. Beyond mechanical performance, the synergistic use of DTPA–5Na and FGD gypsum also regulates the setting behaviour of the BOF slag-based binder, offering a more practical and efficient pathway for the co-utilization of BOF slag and FGD gypsum as industrial by-products in building material applications.

For future work, several aspects warrant further investigation. The long-term mechanical performance and durability of the developed binder system should be systematically evaluated. In addition, a more precise characterization of the C-S-H gel composition and the amorphous phase evolution would improve the accuracy of the theoretical volume and water demand models proposed in this study. The cost-effectiveness of the DTPA–5Na and FGD gypsum combination relative to conventional high-dosage chelator systems also merits quantitative assessment under varying regional material cost conditions. Finally, scaling up the binder system to pilot or field applications represents an important step toward practical implementation.

5. Conclusion

This study investigates the use BOF slag to develop a sustainable cement-free binder activated by DTPA–5Na and modified with FGD gypsum. Hydration kinetics, mechanical performance and environmental impact were evaluated. In addition, the evolution of phase composition, pore structure and microstructure under varying dosages of DTPA–5Na and FGD gypsum dosages was analysed to clarify the underlying mechanisms. The main conclusions can be drawn as follows:

- DTPA–5Na effectively enhances BOF slag hydration. At 1.0 wt%, the cumulative heat release increases from 29.6 J/g to 52.4 J/g (168 h). and 28 d compressive strength improves from 9.4 MPa to 22.5 MPa. This is attributed to the chelation-driven dissolution of brownmillerite, promoting monocarboaluminate formation.
- The incorporation of FGD gypsum delays early hydration and prolongs setting time (from 0.5 h to 2.5 h with 3.5 wt% FGD gypsum) due to partial chelator occupation by Ca^{2+} . Nonetheless, it promotes ettringite formation, refines the microstructure and enhances 28 d compressive strength from 22.5 MPa for D1.0F0–35.8 MPa for D1.0F3.5.
- The developed BOF slag-based binders meet leaching requirements for heavy metals (Co, Cr, Cu, Mo, Ni, and V). However, higher activation levels of BOF slag may increase the release of embedded metals, highlighting the need to balance hydration degree and potential leaching risk.
- The developed BOF slag hydration model indicates its low water demand (0.22–0.26, water-to-binder_{slag} ratio), and low chemical

shrinkage (2.1–3.9 ml/100 g_{slag}), suggesting its advantage in volume stability.

- Sulphate addition is critical for ettringite and hydrocalumite formation, promoting early strength. This process simultaneously accelerates BOF slag dissolution by lowering Ca saturation through precipitation reactions. This supports the use of sulphate-rich industrial residues wastes in BOF slag-based binders to improve performance and enable circular resource utilization.

CRediT authorship contribution statement

Xuan Ling: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Zhihan Jiang:** Writing – review & editing, Methodology, Investigation. **Katrin Schollbach:** Writing – review & editing, Supervision, Conceptualization. **Brouwers H.J.H:** Writing – review & editing, Supervision.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.conbuildmat.2026.147599](https://doi.org/10.1016/j.conbuildmat.2026.147599).

Data availability

Data will be made available on request.

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