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Modeling and experimental validation of carbonation mechanism of ye'elimite-gypsum-water system

Yangyang Zhang · Qunli Zhang · Jun Chang · Hang Yang · Siqi Ding · Xiaozhou Liu · Kai Wu · Qingxin Zhao

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Abstract Calcium sulfoaluminate cement is a promising low-carbon alternative to Portland cement, and the carbonation of its hydration products influences its mechanical performance. However, a comprehensive theoretical model describing its carbonation mechanism remains elusive. This paper established a theoretical reaction range, including different zones and boundaries for ye'elimite (C_4A_3S)-gypsum (CSH_2)-water (H_2O)-carbon dioxide (CO_2) system via priority-based theoretical calculations of chemical reactions. The reactions and product evolution within each boundary and zone were summarized. A theoretical database was obtained, including the change of Gibbs energy and enthalpy, solid volume and chemical volume, and the theoretical carbon absorption.

Y. Zhang · Q. Zhang · H. Yang · Q. Zhao State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

Y. Zhang · Q. Zhang · H. Yang · Q. Zhao Hebei Province Engineering Research Center for Harmless Synergistic Treatment and Recycling of Municipal Solid Waste, Yanshan University, Qinhuangdao 066004, China

Y. Zhang

Hebei High Performance Building Material Technology Innovation Center, Qinhuangdao Municipal Building Materials Group Co. Ltd, Qinhuangdao 066000, China

J. Chang

School of Civil Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

Calculation results reveal that the reactions of each zone and boundary occur spontaneously and exothermically. The solid volume increases, while the chemical volume decreases conversely. The maximum carbon absorption of 1 mol C_4A_3S is 3 mol theoretically regardless of the amount of gypsum. The modeling obtained by Gibbs Energy Minimization software (GEMS-PSI) and experimental verification were carried out to validate the fidelity of the established theoretical reaction range, which demonstrate that the evolution of carbonation products in each zone and boundary was in line with the theoretical calculations. Compared with GEMS modeling, the theoretical reaction range can distinguish the source of ettringite

S. Ding (🖂)

Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China e-mail: s.q.ding@connect.polyu.hk

X. Liu

College of Urban Transportation and Logistics, Shenzhen Technology University, Shenzhen 518118, China

K. Wu (🖂)

Key Laboratory of Advanced Civil Engineering Materials of Ministry of Education, School of Materials Science and Engineering, Tongji University, Shanghai 201804, China

e-mail: wukai@tongji.edu.cn

in detail, and provide a more direct and insightful representation of carbonation process.

Keywords Calcium sulfoaluminate cement \cdot Carbonation \cdot Ye'elimite \cdot Modeling \cdot Database

1 Introduction

Portland cement (PC) stands as the most-commonly used cement type in modern engineering applications [1–3]. During its manufacturing, substantial CO_2 emissions are incurred due to the calcination of limestone with the huge amount of fuel combustion and electricity consumption [4–6]. Therefore, it becomes imperative to propose effective strategies for reducing CO_2 emissions from the cement industry, such as decreasing fuel consumption, improving production efficiency, and reducing calcium carbonate during clinker production, etc.[3, 7, 8].

Calcium sulfoaluminate (CSA) cement is a plausible alternative to Portland cement (PC) due to 200 °C lower calcination temperature of CSA clinker, 40% less CO₂ emissions, and easier clinker grinding compared to PC [9–11]. In addition, CSA cement is highly suitable for engineering applications due to its excellent cementitious properties. For example, the fast setting and hardening properties make it suitable for emergency repairing works [12, 13]. The presence of ettringite in the hydration products renders it wellsuited for shrinkage compensation construction [14, 15]. Moreover, the outstanding frost resistance and impermeability extend its applicability to a wide range of marine engineering applications [16, 17]. CSA cement clinker is mainly composed of ye'elimite (C_4A_3S) combined with other phases including ferrite and belite. The hydration products of $C_4A_3\overline{S}$ consist of monosulfate $(C_4 A \overline{SH}_{12})$ and aluminum hydroxide gel (AH_3) (Eq. (1)) [18–20]. When compounded with a specific amount of gypsum (CSH₂), C_4A_3S reacts with gypsum to generate ettringite ($C_6AS_3H_{32}$, abbreviated as AFt) and AH₃ (Eq. (2)) [21-23]. $(C = CaO; A = Al_2O_3; \overline{S} = SO_3; H = H_2O; \overline{C} = CO_2)$

$$C_4 A_3 S + 18H \rightarrow C_4 ASH_{12} + 2AH_3 \tag{1}$$

$$C_4 A_3 \overline{S} + 2C \overline{S} H_2 + 34H \rightarrow C_6 A \overline{S}_3 H_{32} + 2AH_3 \qquad (2)$$

In the context of low-carbon cement, there has been increasing attention on the carbonation of CSA



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cement in recent years. Traditionally, carbonation has been perceived as a detrimental process for concrete durability [24, 25]. However, the application of accelerated carbonation as a curing method has been proposed for sustainable development of cement production [26, 27]. This is because that there is a competitive occurrence of carbonation and hydration reactions prior to complete cement hydration in the early-age carbonation [28, 29]. Recently, wet carbonation is has been demonstrated to be more efficient in comparison with dry carbonation [30–35]. For instance, Shen et al. [36] applied a two-step wet carbonation to the synthesis of nano-silica from recycled concrete fines (RCF), and enabled RCF to uptake larger amount of CO₂.

The diverse hydration products of CSA cement and PC make a great difference to their carbonation [37-39]. Many studies have reported that CSA cement is more liable to natural carbonation than PC [40–42]. The natural carbonation rates and depths in CSA cement are affected by the water to cement ratio (w/c) [43, 44]. In general, the natural carbonation rate of CSA cement increases with increasing w/c [45]. Table 1 provides a literature summary of carbonation on the mechanical properties of different CSA cement systems. It can be seen that many factors (such as the methods of carbonation, the nature of raw materials in CSA cement, and w/c) would have different impacts on the CSA cement's mechanical properties after carbonation. Additionally, the carbonation of CSA cement blended with supplementary cementitious materials (SCMs) has also been studied [46-54]. Therefore, earlier studies have provided preliminary insights into the carbonation products and the corresponding mechanical influence on CSA cements. However, limited attention has been directly focused on the carbonation of $C_4A_3S-CSH_2-H_2O$, which is the basic reaction system in CSA cement. And no guidelines have been established regarding the theory reaction range of $C_4A_3S-CSH_2-H_2O-CO_2$ system, the corresponding basic thermodynamic database, and validation.

Our work is aiming to bridge the gap from the carbonation of the complex CSA cement system to the mineral phase of ye'elimite, thereby contributing to a fundamental theoretical framework for comprehending the carbonation mechanism of CSA cement. By theoretical calculations, the carbonation process can be explained more scientifically for the complicated

CSA cement system	Carbonation methods	Influence on the mechanical properties	References
CSA clinker with different anhydrite content (binary system) and CSA clinker with different anhydrite content and limestone Porland Cement (ternary system)	The pastes were stored under water for 28d and exposed to two kinds of carbonation, including atmospheric carbonation at 20° C and 60% R.H (indoor environment with $0.05-0.1\%$ CO ₂ concentration) and accelerated carbonation at 20° C (carbonation chamber set as 4% CO ₂ concentration, respectively) for further days	Compressive strength of the binary system was reduced. Compressive strength of the ternary system was improved	Bertola et.al [51]
CSA cement with different w/c of 0.4, 0.5, 0.6 and 0.7	Samples after demolding were placed directly in a carbonation chamber with 10% CO ₂ concentration for 28d curing	A coherent improvement in strength was found in 14d-CO ₂ curing in comparison with water curing, in spite of w/c. Increasing w/c led to strength diminution under water curing	Sharma et.al [52]
CSA cement with three w/c of 0.45, 0.58 and 0.78	Standardized environment and CO ₂ saturated environment were established to cure samples for further 28d after 28d standard curing	For w/c = 0.58 , CO ₂ curing reduced the strength. For w/c = 0.45 , the compressive strength was improved after carbonation. However, carbonation reduced long-term mechanical strength of three CSA samples	Mechling et.al [53]
Modified CSA (MCSA) prepared by superseding fine CSA mortar from 0 to 30 wt%	MCSA mortars were placed in curing chamber for 28d, and then stored in carbonation chamber with 99.9% concentration CO_2 in constant 0.2 MPa pressure	Compressive strength of MCSA was diminished after subjected to accelerated carbonation MCSA with 20% CSA mortar appeared maximum compressive and flexural strength	Ansari et.al [55]
CSA clinker and anhydrite (CS) with different CS7 $C_4A_3\tilde{S}$ ratios of 1, 1.4 and 1.8, and with different w/c of 0.65, 0.525, and 0.4	Demolded prisms were stored in covered mold at 95% R.H. for 3d, and at 57% R.H. for further 25d before accelerated carbonation. The prepared prisms were then stored in a carbonation chamber with 4% CO ₂ concentration	After accelerated carbonation, for w/c = 0.65, the total porosities were increased in the CSA mortars with all the CS/C ₄ A ₃ S ^T ratio; for w/c = 0.65 and 0.525 with the ratio of CS/C ₄ A ₃ S ⁼ 0.4, their compressive strength decreased; for w/c = 0.4 with the same condition, its compressive strength was improved by 5%	Hargis et.al [56]
CSA samples with different CS/C_4A_3S ratios of 1.0, 1.5 and 2.0	After stored in a curing chamber for 28d (70% R.H, 20°C), the samples were carbonated with 3% CO_2 concentration for 28d at 25°C and 50% R.H	Compressive strength was increased for all the three samples	Seo et al.[57]

 Table 1
 Literature summary of carbonation on the mechanical properties of different CSA cement systems

carbonation system in CSA cement and the experimental data can be elucidated. Consequently, this study focused on the establishment of the theory reaction range for C_4A_3S -CSH₂-H₂O-CO₂ system via theoretical calculations. In addition, the volume change and carbon absorption of this system were calculated. Finally, the validation of the theory carbonation range was carried out experimentally assisted by GEMS modeling. Also, by the investigation of C_4A_3S -CSH₂-H₂O carbonation over various time, the microstructure changes of aluminum hydroxide and calcium carbonate can be revealed, offering further insight into the mechanical properties of carbonated CSA cement.

2 Materials and methods

2.1 Preliminary calculations

As reported previously [56], during the carbonation of C_4A_3S , monosulfate is initially carbonated, and converted into monocarbonate and ettringite (Eq. (3)). Once monosulfate is depleted, the monocarbonate $(C_4A\overline{C}H_{11})$ reacts with CO₂ (Eq. (4)). Ettringite is the last phase to be carbonated (Eq. (5)). During the carbonation of monosulfate and ettringite, ettringite from Eq. (3) reacts with CO₂ completely (Eq. (5)). These equations are the basis for the establishment of theoretical carbonation range.

$$6C_4 A\overline{S}H_{12} + 3\overline{C} + 28H \rightarrow 2C_6 A\overline{S}_3 H_{32} + 3C_4 A\overline{C}H_{11} + AH_3$$
(3)

$$C_4 A \overline{C} H_{11} + 3 \overline{C} \to 4 C \overline{C} + 8 H + A H_3 \tag{4}$$

$$C_6 A \overline{S}_3 H_{32} + 3 \overline{C} \rightarrow 3 C \overline{C} + A H_3 + 3 C \overline{S} H_2 + 23 H$$
 (5)

$$C_4 A \overline{S} H_{12} + 3 \overline{C} \to 3 C \overline{C} + A H_3 + C \overline{S} H_2 + 7 H$$
 (6)

Supposing that a hypothetical reaction system contains 1 mol of $C_4A_3\overline{S}$, *a* mol of $C\overline{SH}_2$ and *b* mol of CO_2 , and another system contains 1 mol of $C_4A_3\overline{S}$, *a* mol of $C\overline{SH}_2$ and enough water. When complete hydration occurs, all reactants participate in the reaction without surplus. To illustrate this, a theoretical reaction range is established, where the horizontal



axis represents the amount of CSH_2 , and the vertical axis represents the amount of CO_2 .

As shown in Fig. 1, there are some specific coordinate points in the theoretical reaction range of the $C_4A_3\overline{S}$ - $C\overline{SH}_2$ - H_2O - CO_2 system, at which reactions would be taken place according to Eqs. (1–6). These points form distinct boundaries, namely Bottom boundary (BB), Boundary I (BI), Boundary II (BII), Boundary III (BIII), Top boundary (TB), Left boundary (LB), and Right boundary (RB). The boundaries divide the theoretical reaction range into different zones, i.e., Zone I, Zone II, Zone III, and Zone IV, as summarized in Tables 2, 3 and 4.

2.2 Modeling

The modeling of C_4A_3S - CSH_2 - H_2O - CO_2 system was performed using Gibbs Energy Minimization software (GEMS-PSI), based on the PSI-Nagra database and Cemdata18 database [58, 59]. The C_4A_3S - CSH_2 - H_2O system was first simulated by adding 1 mol C_4A_3S , along with a certain quantity of water and different quantities of gypsum (1/2, 1, 3/2 mol). The quantity of CO_2 in this modeling ranged from 0 to 200 g, and the entire system was virtually titrated with a small quantity of O_2 .

2.3 Experimental validation

2.3.1 Sample preparation

The experiment was divided into two main parts: a hydration experiment of C_4A_3S and a carbonation experiment. First, C_4A_3S was synthesized by stoichiometric mixture of analytical grade chemicals in a planetary mill for 10 min, including calcium sulfate (CaSO₄), aluminum oxide (Al₂O₃) and calcium carbonate (CaCO₃). The dried materials were sintered in a laboratory electric furnace at 1300°C for 4 h. After cooling, the sintered C_4A_3S clinker was ground to pass a sieve with an 80 µm-mesh, and exhibited a purity of 96.7%, with the remaining components of 0.8% CaO and 2.5% C₁₂A₇.

Then, hydration experiments were carried out by mixing C_4A_3S and CSH_2 , with two molar ratios of 0 and 2 representing LB and RB. Moreover, a high water-solid ratio of 10 and a curing time of 28d was utilized for full hydration. After mixing powder and water, different samples of slurries were dispersed



Fig. 1 Evolution of reactants and products in the theoretical reaction range.

 Table 2 Definitions of different coordinate points

Coordinate point	Definition
(0, 0)	1 mol $C_4A_3\overline{S}$ hydrates, forming 1 mol monosulfate and 2 mol AH_3 , as dictated by Eq. (1)
(2,0)	2 mol CSH_2 in the system, resulting in the formation of ettringite and AH ₃ , as dictated by Eq. (2)
(0, 1/2)	$1/2 \text{ mol CO}_2$ in the system and reaction occurs according to Eqs. (1) and (3) since monosulfate will firstly react with CO ₂ to generate monocarbonate in Eq. (3)
(0, 2)	2 mol CO_2 is consumed according to Eqs. (3) and (4)
(0, 3)	System would react according to Eqs. (1) and (3-5)
(2, 3)	At the point (2, 0), the amount of formed ettringite is 1 mol, and then it will carbonate according to Eq. (5), thus 3 mol CO_2 is consumed

with ultrasonic dispersion instrument at room temperature (20 °C). After 28d, the filtered samples were immersed with isopropanol for 15 min first and rinsed with diethyl ether. Ultimately, they were dried at 40 °C for 8 min in a vacuum dryer. The Rietveld methodology was used to analyzed the content of hydration products by using TOPAS 4.2 software. For pure hydration of C₄A₃ \overline{S} , no C₄A₃ \overline{S} remained after 28 days, with 54.2 wt.% monosulfate generated, illustrating complete hydration of C₄A₃ \overline{S} . For hydration of C₄A₃ \overline{S} and 2 mol CSH₂, after 28d, C_4A_3S has completely hydrated with CSH_2 , and 70.1 wt.% ettringite was generated.

In the carbonation experiment, a wet carbonation method was applied by mixing the dried powder and water with water-solid ratio of 20. Moreover, the speed of the magnetic stirrer was maintained at 200 rpm, and a flowmeter for carbon dioxide gas cylinders was kept at 175 mL/min. Samples after carbonation for various time were filtered to remove water and immersed in isopropanol for 15 min. All



Table 3 Definitions of different boundaries

Boundary	Definition
BB	It extends from point (0, 0) to point (2, 0), representing the system of $C_4A_3S-CSH_2$. In the presence of CO_2 , monosulfate carbonates firstly
BI	It extends from point $(0, 1/2)$ to point $(2, 0)$, indicating the sole occurrence of Eq. (3)
BII	It extends from point $(0, 2)$ to point $(2, 0)$, indicating the occurrence of Eqs. (3) and (4)
BIII	It extends from point $(0, 3)$ to point $(2, 0)$, corresponding to a scenario in which all ettringite generated from Eq. (3) has precipitated within the solution
ТВ	It extends from point (0, 3) to point (2, 3), in which all the reactants are completely carbonated, including monosulfate, monocarbonate and ettringite from two parts
LB	It extends from point $(0, 0)$ to point $(0, 3)$, indicating the carbonation of monosulfate in accordance with Eq. (6) along with the complete reaction of the ettringite generated from Eq. (3) with CO ₂ , as described in Eq. (5)
RB	It extends from point (2, 0) to point (2, 3), representing the carbonation of ettringite from hydration products of C_4A_3S and gypsum (Eq. (5))

Table 4 Definitions of different zones

Zone	Definition
Zone I	It is positioned beneath BI and experiences the incomplete carbonation of monosulfate (Eq. (3)), due to the insufficient amount of CO ₂
Zone II	It is between BI and BII, representing the complete carbonation of monosulfate according to Eq. (3), with monocarbonate generated and subsequently reacting partially with CO_2
Zone III	It is between BII and BIII, indicating the partial occurrence of Eq. (5)
Zone IV	It is beyond BIII in which the amount of CO_2 is enough to facilitate the carbonation of ettringite from the hydration products of C_4A_3S and gypsum

samples were dried at 40 °C for 8 min in a vacuum dryer.

2.3.2 Characterization

X-ray diffraction analysis (XRD) was performed using a Bruker D8 ADVANCE diffractometer equipped with CuK $\alpha_{1,2}$ radiation, operating at 40 mA and 40 kV. The step size used in this experiment was 0.02° 20 with 0.5 s per step in the 5–80° 20 range.

Thermogravimetry and derivative thermogravimetry (TG-DTG) test was carried out using a Mettler Toledo TGA/DSC instrument. The experiment was performed from 50 to 1000 °C at a heating rate of 10 °C/min under a continuous N_2 flow to prevent carbonation.



3 Results and discussion

3.1 Thermodynamic calculation

From the calculations (see Appendix), it can be concluded that the hydration reactions and carbonation reactions of Boundaries I-III and TB occur according to Eqs. (7, 8) and Eqs. (9–12), respectively. The hydration reaction of Eq. (8) occurs in all of the zones. Besides Eq. (8), the hydration reactions of Zones I-IV are also taken place according to Eq. (13), Eq. (15), Eq. (18), and Eq. (21). As for the carbonation reactions of each zone, Eq. (14) occurs in Zone I; Eqs. (16) and (17) take place in Zone II; Eqs. (19) and (20) occur in Zone III; Eqs. (22) and (23) take place in Zone IV. The reactions

Table 5 Equations occurred in each boundary and zone

Equations
Equations (7) (8)
Equations (8) (13) (14)
Equations (7) (8) (9)
Equations (8) (15) (16) (17)
Equations (7) (8) (10)
Equations (8) (18) (19) (20)
Equations (7) (8) (11)
Equations (8) (21) (22) (23)
Equations (7) (8) (12)

of each boundary and zone are summarized in Table 5. In addition, it should be noted that the theoretical calculations in this work characterize thermodynamical equilibriums.

$$(1 - \frac{a}{2})C_4A_3\overline{S} + (18 - 9a)H \to (1 - \frac{a}{2})C_4A\overline{S}H_{12} + (2 - a)AH_3$$
(7)

$$\frac{a}{2}C_{4}A_{3}\bar{S} + aC\bar{S}H_{2} + 17aH \rightarrow \frac{a}{2}C_{6}A\bar{S}_{3}H_{32} + aAH_{3}$$
(8)

$$\begin{pmatrix} 1 - \frac{a}{2} \end{pmatrix} C_4 A \bar{S} H_{12} + \left(\frac{1}{2} - \frac{a}{4}\right) \bar{C} + \left(\frac{14}{3} - \frac{7a}{3}\right) H \rightarrow \left(\frac{1}{3} - \frac{a}{6}\right) C_6 A \bar{S}_3 H_{32} + \left(\frac{1}{2} - \frac{a}{4}\right)$$

$$C_4 A \bar{C} H_{11} + \left(\frac{1}{6} - \frac{a}{12}\right) A H_3$$

$$(9)$$

$$\begin{pmatrix} 1 - \frac{a}{2} \end{pmatrix} C_4 A \bar{S} H_{12} + (2 - a) \bar{C} + \left(\frac{2 - a}{3}\right) H \rightarrow \left(\frac{1}{3} - \frac{a}{6}\right) C_6 A \bar{S}_3 H_{32} + (2 - a) C \bar{C} + \left(\frac{2 - a}{3}\right) A H_3$$
 (10)

$$2\left(1-\frac{a}{2}\right)C_{4}A\bar{S}H_{12} + \left(3-\frac{3a}{2}2\right)\bar{C} \to 2\left(3-\frac{3a}{2}\right)C\bar{C} + \left(1-\frac{a}{2}\right)AH_{3} + \left(1-\frac{a}{2}\right)C\bar{S}H_{2} + \left(7-\frac{7a}{2}\right)H$$
(11)

$$\frac{a}{2}C_6A\overline{S}_3H_{32} + \frac{3a}{2}\overline{C} \rightarrow \frac{3a}{2}C\overline{C} + \frac{a}{2}AH_3 + \frac{3a}{2}C\overline{S}H_2 + \frac{23a}{2}H$$
(12)

$$2bC_4 A_3 \bar{S} + 36bH \rightarrow 2bC_4 A \bar{S}H_{12} + 4bAH_3$$
 (13)

$$2bC_{4}A\bar{S}H_{12} + b\bar{C} + \frac{28b}{3}H \to \frac{2b}{3}C_{6}A\bar{S}_{3}H_{32} + bC_{4}A\bar{C}H_{11} + \frac{b}{3}AH_{3}$$
(14)

$$\frac{b}{2}C_4A_3\bar{S} + 9bH \to \frac{b}{2}C_4A\bar{S}H_{12} + bAH_3$$
 (15)

$$\frac{b}{2}C_4 A\bar{S}H_{12} + \frac{b}{4}\bar{C} + \frac{7b}{3}H \rightarrow \frac{b}{6}C_6 A\bar{S}_3 H_{32} + \frac{b}{4}C_4$$

$$A\bar{C}H_{11} + \frac{b}{12}AH_3$$
(16)

$$\frac{b}{4}C_4A\bar{C}H_{11} + \frac{3b}{4}\bar{C} \to bC\bar{C} + 2bH + \frac{b}{4}AH_3$$
(17)

$$\frac{b}{3}C_4A_3\bar{S} + 6bH \to \frac{b}{3}C_4A\bar{S}H_{12} + \frac{2b}{3}AH_3$$
 (18)

$$\frac{b}{3}C_4A\bar{S}H_{12} + \frac{2b}{3}\bar{C} + \frac{2b}{9}H \to \frac{b}{9}C_6A\bar{S}_3H_{32} + \frac{2b}{3}C\bar{C} + \frac{2b}{9}AH_3$$
(19)

$$\frac{b}{9}C_{6}A\bar{S}_{3}H_{32} + \frac{b}{3}\bar{C} \to \frac{b}{3}C\bar{C} + \frac{b}{9}AH_{3} + \frac{b}{3}C\bar{S}H_{2} + \frac{23b}{9}H_{3}$$
(20)

$$\left(\frac{b}{3} - \frac{a}{2}\right)C_4 A_3 \bar{S} + (6b - 9a)H \rightarrow \left(\frac{b}{3} - \frac{a}{2}\right)C_4 A \bar{S}H_{12}$$

$$+ \left(\frac{2b}{3} - a\right)AH_3$$

$$(21)$$

$$\left(\frac{b}{3} - \frac{a}{2}\right)C_4A\bar{S}H_{12} + \left(b - \frac{3a}{2}\right)\bar{C} \rightarrow \left(b - \frac{3a}{2}\right)C\bar{C} + \left(\frac{b}{3} - \frac{a}{2}\right)AH_3 + \left(\frac{b}{3} - \frac{a}{2}\right)C\bar{S}H_2 + \left(\frac{7b}{3} - \frac{7a}{2}\right)H$$

$$(22)$$

$$\frac{a}{2}C_{6}A\bar{S}_{3}H_{32} + \frac{3a}{2}\overline{C} \to \frac{3a}{2}C\bar{C} + \frac{a}{2}AH_{3} + \frac{a}{2}C\bar{S}H_{2} + \frac{7a}{2}H$$
(23)

The evolution of reactants and products is shown in Fig. 1, and the quantities of all the reactants and products of each zone and boundary are listed in Table 6. It can be seen that monocarbonate only exists in the Zone I and BI as an intermediate carbonation product. Under these conditions, neither calcium carbonate nor gypsum is formed. The generation of calcium carbonate will begin from Zone III; and in Zone III, gypsum plays a dual role, both as a reactant and a product. In Zone IV and TB, gypsum will play a distinct role as a product rather than a reactant at other regions. As shown in Table 6, the amount of C_4A_3S in each zone is (a/2+2b), (a/2+b/2), (a/2+b/3), and (b/3) mol,



Location	Reactant			Product					
	$\overline{C_4 A_3 S}$	CO ₂	CSH_2	H ₂ O	$\overline{C_6AS_3H_{32}}$	$C_4 A \bar{C} H_{11}$	$C\overline{C}$	AH ₃	CSH ₂
Zone I(0 < b < 1/2-a/4)	a/2+2b	b	a	17a+136b/3	a/2+2b/3	b	0	a+13b/3	0
BI $(b = 1/2 - a/4)$	1	b	а	17a/3+68/3	1-4b/3	b	0	2 + b/3	0
Zone II (1/2-a/4 < b < 2-a)	a/2 + b/2	b	а	17a+28b/3	a/2 + b/6	0	b	a+4b/3	0
BII $(b=2-a)$	1	b	а	23a/3+56/3	1-b/3	0	b	2 + b/3	0
Zone III (2-a < b < 3-3a/2)	a/2 + b/3	b	а	17a+11b/3	a/2	0	b	a+b	b/3
BIII $(b = 3 - 3a/2)$	1	b	а	23a/2+11	1-b/3	0	b	2 + b/3	b/3
Zone IV($3-3a/2 < b < 3$)	b/3	b	0	11b/3	0	0	b	b	b/3
TB(b=3)	1	3	0	11	0	0	3	3	1

Table 6 Number of reactants and products of each boundary and zone

respectively. It is worth noting that in Zone III, the production of ettringite depends on that of gypsum, and remains unaffected by the presence of CO₂; in Zone IV and TB, there is no formation of ettringite. As for calcium carbonate, it is obvious that its number is decided by CO₂ in the case of calcium carbonate generation. Regarding aluminum hydroxide, at Boundaries I-III, its number is (2 + b/3) mol, which will increase with the number of CO₂ in this situation. The amount of the formed aluminum hydroxide in each zone is (a + 13b/3), (a + 4b/3), (a + b) and 3 mol, respectively.

In this section, the calculation of the Gibbs energies and enthalpy in each boundary and zone was carried out to determine whether the total reactions can occur spontaneously. Additionally, calculating the change in enthalpy for each boundary and zone could confirm whether the total reactions in these regions are endothermic or exothermic. Through the thermodynamic calculations for each boundary and zone, thermodynamic databases of C_4A_3S - CSH_2 - H_2O - CO_2 theoretical reaction system can be set up. This serves as a valuable theoretical foundation for future research on carbonation of CSA cement. Standard molar Gibbs energies, enthalpy, and molar volume of each substance are provided in Table 7, wherein the Gibbs energies and enthalpy of AH_3 are twice that of $Al(OH)_3$.

3.1.1 Calculation of Gibbs energy and enthalpy

The change of Gibbs energy and enthalpy of each boundary and zone is summarized in Table 8. Obviously, the change of Gibbs energy and enthalpy of Zone I, BI, Zone II, Zone III, Zone IV and TB is constantly negative, which is because that the value range of a is from 0 to 2 and that of b is 0 to 3. As for Gibbs energies of BII and BIII, when a equals to the maximum value, the change of Gibbs energy and enthalpy of BII is always less than 0. In conclusion, the change of Gibbs energy and enthalpy of each zone and boundary is constantly less than 0, which demonstrates that the total reactions of each boundary and zone are able to occur spontaneously and are exothermic.

Table 7 Standard molar Gibbs energies ΔG^0	Phase	$\Delta_{\rm f} {\rm G}^0/({\rm kJ}~{\rm mol}^{-1})$	$\Delta_{\rm f} {\rm H}^0/({\rm kJ}~{\rm mol}^{-1})$	$V^{0}/(cm^{3} mol^{-1})$	References
enthalpy $\Delta_f H^0$, and molar	$\overline{C_4A_3S}$	- 8078.00	- 8513.00	242.60^{1}	[60]
volume V ⁶	CSH_2	- 1797.76	-2023.36	75.00	[<mark>61</mark>]
	$C_6 A \overline{S_3} H_{32}$	-15,205.94	-17,535.00	707.00	[<mark>61</mark>]
1	Al(OH) ₃	-1148.40	- 1265.30	32.50	[<mark>61</mark>]
¹ Calculated by the ratio of molar mass to density and	$C_4 A \overline{C} H_{11}$	-7337.46	- 8250.00	262.00	[<mark>61</mark>]
value of density is from	H ₂ O	-237.18	-286.00	18.00	[<mark>61</mark>]
[63]	CO_2	- 386.02	-413.84	-	[<mark>61</mark>]
² Calcium carbonate is regarded as calcite	$C\overline{C}^2$	- 1129.18	- 1207.60	37.00	[62]



 Table 8
 Calculation of Gibbs energy and enthalpy change of each boundary and zone

Location	$\Delta G/(kJ mol^{-1})$	$\Delta H/(kJ mol^{-1})$
Zone I $(0 < b < 1/2 - a/4)$	- 30.8a-46.7b	- 156.2a-500.8b
BI $(b = 1/2 - a/4)$	-23.4-19.1a	-251-31a
Zone II (1/2- a/4 < b < 2-a)	- 31a-87.2b	– 156.4a–164.7b
BII $(b=2-a)$	- 174.1 + 56.2a	-329.4+8.3a
Zone III $(2-a < b < 3-3a/2)$	– 1828.7a-76.9b	-2179.6a-112.5b
BIII $(b=3-3a/2)$	-230.7+84.4a	- 337.5 + 112.5a
Zone IV (3-3a/2 < b < 3)	-76.7b	-113.6b
TB $(b=3)$	-230	-340.9

3.1.2 Calculation of chemical and solid volume change

Solid and chemical volume change of each zone and boundary are shown in Table 9 and Table 10. Solid volume will increase in each boundary and zone because of the formation of ettringite from carbonation reactions. Even in the absence of ettringite

 Table 9
 Solid volume change in the theoretical carbonation range

formation in Zone IV and TB, solid volume still exhibits an increase trend. Furthermore, it is obvious that chemical volume change within each zone and boundary will decline due to the reduction in water content.

3.1.3 Calculation of carbon absorption

At each boundary, the quantity of C_4A_3S taking part in the carbonation reaction remains constant at 1 mol, which is different from that of each zone. The corresponding CO₂ absorption in each reaction is various as well. As shown in Table 6, the amount of C_4A_3S in Zones I-IV is (a/2+2b), (a/2+b/2), (a/2+b/3)and (b/3) mol and that of CO₂ in each zone is *b* mol. Hence, the ratio of CO₂ to C_4A_3S can be used to describe the carbon absorption of each zone and boundary. Table 11 shows the carbon absorption of each zone and boundary. Moreover, at TB, where complete carbonation of all reactants occurs, the total carbon absorption is 3 mol. Significantly, during the sintering of C_4A_3S , the decomposition of raw material-calcium carbonate tends to occur inevitably,

Location	$Reactant/(cm^3 mol^{-1})$	$Product/(cm^3 mol^{-1})$	Change/($cm^3 mol^{-1}$)	Result
Zone I (0 < b < 1/2-a/4)	196.3a+485.2b	386a+874.2b	189.7a+389b	Increase
BI $(b = 1/2 - a/4)$	242.6+75a	437.1+167.5a	194.5+92.5a	Increase
Zone II (1/2-a/4 < b < 2-a)	196.3a+121.3b	386a+423.2b	189.7a+301.9b	Increase
BII $(b=2-a)$	242.6+75a	846.6–37.2a	604–112.2a	Increase
Zone III (2-a < b < 3-3a/2)	196.3a+80.7b	386a+94.5b	189.7a+13.8b	Increase
BIII $(b=3-3a/2)$	242.1+75.2a	283.5+244.3a	41.4+169.1a	Increase
Zone IV (3-3a/2 < b < 3)	80.9b	94.5b	13.6b	Increase
TB $(b=3)$	242.6	283.5	40.9	Increase

Table 10 Chemical volume change in the theory carbonation range

Location	Reactant/($cm^3 mol^{-1}$)	$Product/(cm^3 ol^{-1})$	Change/($cm^3 mol^{-1}$)	Result
Zone I (0 < b < 1/2-a/4)	502.3a+1301.2b	386a+874.2b	-116.3a-427b	Decrease
BI $(b = 1/2 - a/4)$	650.6+177a	437.1 + 167.5a	-9.5a-213.5	Decrease
Zone II $(1/2-a/4 < b < 2-a)$	502.3a+289.3b	386a+198.2b	-116.3a-91.1b	Decrease
BII $(b=2-a)$	578.6+213a	396.3 + 187.8a	182.3–25.2a	Decrease
Zone III $(2-a < b < 3-3a/2)$	505.3a+146.9b	386a+94.5b	-119.3a-52.4b	Decrease
BIII $(b = 3 - 3a/2)$	440.7+285b	283.5+244.3b	-157.2-40.7b	Decrease
Zone IV $(3-3a/2 < b < 3)$	146.9b	94.5b	- 52.4b	Decrease
TB $(b=3)$	440.6	283.5	- 157.1	Decrease



rendering CO₂ emissions. 3 mol of CO₂ are released for every 1 mol of C₄A₃ \overline{S} sintering. Therefore, in an ideal situation where all the reactants are fully carbonated, the quantity of carbon absorption of C₄A₃ \overline{S} carbonation is equal to that of carbon release during the C₄A₃ \overline{S} sintering.

3.2 Modeling

To examine the validity of the calculations presented above, it is essential to verify the established theoretical carbonation range through experimental validation. However, owing to the complexity of each zone and boundary, the selection of specific boundaries is the only practicable way for validation. Consequently, the left and right boundaries, where the quantity of CSH_2 is 0 and 2 mol, has been selected for experimental validation. As for the other boundaries and zones, a modeling approach was employed for the $C_4A_3S-CSH_2-CO_2-H_2O$ system.

It is evident that the quantity of gypsum plays a pivotal role in influencing the production of both hydration and carbonation products. Therefore, three vertical lines in the theory carbonation range are made to represent the situations of different amounts of gypsum. Specifically, Figs. 2a, 2c, and 2e stand for the conditions where amounts of gypsum are 1/2, 1, and 3/2 mol, respectively. Figures 2b, 2e, and 2f show mass changes of C_4A_3S -CSH₂-H₂O-CO₂ with different amounts of gypsum (1/2, 1, and 3/2 mol) in the case of complete hydration of 1 mol C_4A_3S .

In the condition of 1/2 mol gypsum (Fig. 2b), it can be seen that at line $i_{1/2}$, monosulfate undergoes complete reaction with CO₂, and the amount of generated

 Table 11
 Carbon absorption of each zone and boundary

Location	Carbon absorption (mol)
Zone I (0 < b < 1/2-a/4)	2b/(a+4b)
BI $(b = 1/2 - a/4)$	1/2-a/4
Zone II $(1/2-a/4 < b < 2-a)$	2b/(a+b)
BII $(b=2-a)$	2-a
Zone III $(2-a < b < 3-3a/2)$	6b/(3a+2b)
BIII $(b = 3 - 3a/2)$	3-3a/2
Zone IV $(3-3a/2 < b < 3)$	3
TB $(b=3)$	3



monocarbonate begins to decrease, when the amount of CO₂ reaches 16.5 g. In this case, the amount of CO_2 is 3/8 mol, corresponding to point (1/2, 3/8) at BI in Fig. 2a. The vertical line from (1/2, 0) to (1/2, 0)3/8) can represent the zone where the amount of CO₂ increases from 0 to 1/2 mol in Fig. 2b. Also, when monocarbonate reacts with CO₂ completely (line $ii_{1/2}$), the amount of CO₂ is 66 g (3/2 mol), and thus point (1/2, 3/2) at BII in Fig. 2a can represent line $ii_{1/2}$ in Fig. 2b. The vertical line from point $i_{1/2}$ to $ii_{1/2}$ in Fig. 2a corresponds to the zone from line $i_{1/2}$ to $ii_{1/2}$ in Fig. 2b as well. At line $iii_{1/2}$, the amount of CO₂ is 132 g (3 mol), all of monosulfate and ettringite are entirely carbonated, corresponding to point (1/2, 3) at TB in Fig. 2a. The vertical line from point $ii_{1/2}$ to $iii_{1/2}$ in Fig. 2a corresponds to the zone from line $ii_{1/2}$ to $iii_{1/2}$ in Fig. 2b as well. When the amount of gypsum is 1 mol (Fig. 2d), 11 g CO₂ (1/4 mol) will be consumed in the case of complete carbonation of monosulfate, which represents point (1, 1/4) in Fig. 2c. The vertical line from (1, 0) to (1, 1/4) in Fig. 3c corresponds to the zone where the amount of CO_2 increases from 0 to 1/4 mol in Fig. 3d. Complete carbonation of monocarbonate will consume 44 g CO₂ (1 mol) at line ii_1 , which represents point (1, 1) in Fig. 2c. The vertical line from point i_1 to ii_1 in Fig. 2c corresponds to the zone from line i_1 to ii_1 in Fig. 2d. At line iii₁, the amount of CO_2 is 132 g (3 mol) and it stands for point (1, 3) at BIII in Fig. 2c. The vertical line from point ii₁ to iii_i in Fig. 2c corresponds to the zone from line ii_1 to iii_1 in Fig. 2d. When the amount of gypsum is 3/2 mol (Fig. 2f), it can be seen from Fig. 2f that when monosulfate totally carbonates (line $i_{3/2}$), the amount of CO₂ is 5.5 g (1/8 mol) and it corresponds to point (3/2, 1/8) at BI in Fig. 2e. The vertical line from (3/2, 0) to (3/2, 1/8) can represent the zone where the amount of CO₂ increases from 0 to 1/8 mol in Fig. 2e. Also, when monocarbonate totally reacts with CO_2 at line $ii_{3/2}$, the amount of CO_2 is 22 g (1/2 mol), which represents point (3/2, 1/2) at BII in Fig. 2e and the line from point $ii_{3/2}$ to $iii_{3/2}$ in Fig. 2e can represent the zone between line $ii_{3/2}$ and $iii_{3/2}$. At line $iii_{3/2}$, it can be denoted by point (3/2, 3) at BIII in Fig. 2e.

The theoretical reaction range, established through thermodynamic calculations, defines boundary I (complete carbonation of monosulfate), boundary II (complete carbonation of monocarbonate), and the top boundary (complete carbonation of ettringite), corresponding to Eqs. (3), (4), and (6), respectively. These boundaries are represented as distinct vertical lines in the modeling results. Under conditions of incomplete carbonation, the CO_2 amount is below these critical thresholds, represented by distinct zones within the theoretical reaction range. This demonstrates the capacity of the theoretical reaction range, derived from thermodynamic calculations, to accurately represent the modeling results obtained for varying gypsum dosages.

In the modeling framework, with a fixed gypsum content, variations in carbonation products are solely dependent on the amount of CO₂. While theoretically, infinite gypsum dosages could generate infinite modeling results and corresponding phase diagrams, this approach becomes computationally challenging when considering both CO₂ and gypsum as independent variables within GEMS modeling. The theoretical reaction range effectively addresses this limitation by incorporating both CO₂ and gypsum quantities. By consolidating these potential infinite modeling results into defined boundaries and zones, the theoretical reaction range provides a more comprehensive and insightful representation of the carbonation process. This significantly justifies the use of the theoretical reaction range, derived from fundamental thermodynamic principles.

It is important to note that the modeling results do not distinguish the origin of ettringite (i.e., whether it originates from monosulfate carbonation or $C_4A_3\overline{S}$ hydration). Consequently, the modeling results do not clearly define distinct boundaries for ettringite carbonation in Figs. 2b, 2d, and 2f. The theoretical reaction range addresses this limitation explicitly differentiating the carbonation by pathways of ettringite from these two sources. Specifically, boundary III, derived from theoretical calculations, characterizes the carbonation of ettringite formed via Eq. (3). Generally, the boundaries of the theoretical carbonation range, with the exception of boundary III, can be represented by points generated from C₄A₃S-CSH₂- H_2O-CO_2 modeling with varying $C_4A_3\overline{S:}C\overline{SH}_2$ ratios. The zones within the theoretical reaction range can be further subdivided into infinite vertical lines representing different gypsum amounts. These vertical lines correspond to the zones observed in the modeling results, except for Zone III.

3.3 Experiments

3.3.1 Carbonation of the left boundary (LB)

Figure 3a shows the XRD results of LB. After carbonated for 5 min, the carbonation products were identified as monosulfate, monocarbonate, vaterite, aragonite, and aluminum hydroxide. This indicates that monosulfate was carbonated according to Eq. (3), forming monocarbonate, ettringite, and aluminum hydroxide. The generated monocarbonate carbonated partly according to Eq. (4), leading to the formation of calcium carbonate. Then, after 10 min of carbonation, there was no longer monocarbonate generated in this condition, indicating the complete carbonation of monocarbonate (Eq. (4)). It is worth noting that in this condition, no gypsum was detected, indicating the ettringite has not yet undergone carbonation. After 20 min of carbonation, gypsum was detected, indicating the carbonation of ettringite occurred and calcium carbonate was formed. In this case, in addition to calcite and vaterite, the peak of aragonite was also detected. Finally, after 40 min of carbonation, neither monosulfate nor ettringite was detected. This indicates the complete carbonation of both phases. The final carbonation products were gypsum, vaterite, calcite, aragonite, and aluminum hydroxide.

TG-DTG results of the LB and the associated mass loss of aluminum hydroxide and calcium carbonate are show in Fig. 3b and 3c. It can be seen from Fig. 3b that monosulfate content exhibited a gradual decline with prolonged carbonation time. After carbonated, the peaks of gypsum and ettringite were identified. Also, as the carbonation time prolonged, the mass loss of aluminum hydroxide and calcium carbonate continuously increased (Fig. 3c), corresponding to an increase in the content of these two products, which is agreement with the calculation results (Fig. 3d).

3.3.2 Carbonation of the right boundary (RB)

Figure 4a shows the XRD result of right boundary. It is evident that after 5 min of carbonation, carbonation of ettringite occurred according to Eq. (5), and thus gypsum, calcium carbonate, and aluminum hydroxide were formed. The peaks of aragonite and vaterite were also detected. After 10 min of carbonation, the carbonation products remained gypsum, calcium





<Fig. 2 Theoretical carbonation range with different vertical lines, **a** $CSH_2=1/2$ mol; **c** $CSH_2=1$ mol; **e** $CSH_2=3/2$ mol. Modeling results of $C_4A_3S^-CSH_2-H_2O-CO_2$ with different ratios of $C_4A_3S^-$ and CSH_2 , **b** $C_4A_3S/CSH_2=1/2$; **d** $C_4A_3S/CSH_2=1/2$; **d** $C_4A_3S/CSH_2=3/2$.

carbonate, and aluminum hydroxide. In the condition of 15 min, ettringite was completely carbonated since no peak of ettringite was detected in this case, and this contributed to the formation of gypsum, aragonite, vaterite, and aluminum hydroxide. Therefore, carbonation of ettringite occurs according to Eq. (5) to generate gypsum, calcium carbonate. and aluminum hydroxide.

TG-DTG results for the RB are presented in Fig. 4b, and the associated mass loss of aluminum hydroxide and calcium carbonate is detailed in Fig. 4c. As observed in Fig. 4b, the mass loss of ettringite gradually decreased with the increasing carbonation time, and the mass loss peak of gypsum was observed meanwhile. Also, the mass loss of aluminum hydroxide and calcium carbonate gradually increased after carbonation for 5, 10 and 15 min, consistent with the calculation results (Fig. 4d).

In conclusion, the experiment results for the left boundary demonstrate that with the increasing amount of CO_2 , Eq. (3) occurs first and the generated monocarbonate carbonates according to Eq. (4). Then, ettringite begins to carbonate according to Eq. (5), and upon complete carbonation of both monosulfate and ettringite, the carbonation products are gypsum, calcium carbonate, and aluminum hydroxide. With the increasing carbonation time, the content of calcium carbonate and aluminum hydroxide increased, which were corresponding with calculation results. In the case of the right boundary, when carbonation of ettringite occurs, only Eq. (5) takes effect. With the increasing amount of CO_2 , the carbonation products are constantly calcium carbonate, gypsum, and aluminum hydroxide until ettringite is completely consumed and their content increased gradually, which were in line with calculation results. Furthermore, the differences observed between experimental results and the two calculation methods may be attributed to reaction kinetics and the evolution of porosity, which affects diffusion and can be influenced by carbonate precipitation. These aspects will be the focus of future research.

4 Conclusions

In this paper, the theory carbonation range of $C_4A_3\overline{S}$ - $C\overline{S}H_2$ - H_2O - CO_2 system was set up, and thermodynamic calculations were conducted. Validation of the theory carbonation range was carried out based on the experimental and modeling results. The conclusions are as follows.

- 1. A theory reaction range of $C_4A_3\overline{S}$ - $C\overline{SH}_2$ - H_2O - CO_2 system was established, with the assumption of 1 mol $C_4A_3\overline{S}$, *a* mol $C\overline{SH}_2$, *b* mol CO_2 , and water within the system. Four zones and seven boundaries were delineated in the carbonation range, each representing the evolution of reactions and carbonation products in each area.
- 2. Thermodynamic calculations including Gibbs energy and enthalpy illustrated that reactions of each boundary and zone were able to occur spontaneously, and these reactions were all exothermic.
- 3. The maximum carbon absorption of $1 \mod C_4 A_3 \overline{S}$ is 3 mol theoretically regardless of the amount of gypsum.
- 4. Solid volume changes in each boundary and zone would increase, and chemical volume changes would decrease theoretically.
- 5. The modeling results illustrated that the evolution of carbonation products in each zone and boundary was in line with the GEMS modeling results. Compared with modeling results, theoretical calculations distinguished the carbonation of ettringite from two sources, and established zone III and boundary III. Moreover, the theoretical calculations provide a more direct and insightful representation of carbonation process by simultaneously considering both CO_2 and gypsum as influencing factors.
- 6. Experiment results of left boundary and right boundary were generally corresponding to the established theory carbonation range.



Fig. 3 a XRD pattern of LB; E: ettringite; M: monosulfate; MC: monocarbonate; G: gypsum; V: vaterite; A: aragonite; C: calcite. b TG-DTG thermograms of LB; c Mass loss of alu-

minum hydroxide and calcium carbonate in TG-DTG thermograms; **d** Calculated molar mass of aluminum hydroxide and calcium carbonate as a function of CO_2 .



Fig. 4 a XRD pattern of RB; E: ettringite; G: gypsum; V: vaterite; A: aragonite **b** TG-DTG thermograms of RB; **c** Mass loss of aluminum hydroxide and calcium carbonate in TG-

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DTG thermograms; **d** Calculated molar mass of aluminum hydroxide and calcium carbonate as a function of CO_2

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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Appendix: Theoretical calculations of the theoretical carbonation range

Boundary

At BB, CSH_2 increases from 0 to 2 mol and thus a certain amount of C_4A_3S reacts with CSH_2 to form ettringite according to Eq. (2) and the other hydrates separately to from monosulfate according to Eq. (1). If the amount of C_4A_3S participating in Eqs. (1) and (2) is set as *x* mol and *y* mol, the amount of C_4A_3S participating in Eqs. (1) and (2) is calculated as (1-a/2) and (a/2) mol, as deducted in Eqs. (24) and (25).

$$\begin{cases} x+y=1\\ 2y=a \end{cases}$$
(24)

$$\begin{cases} x = 1 - a/2\\ y = a/2 \end{cases}$$
(25)

At BI, when CO₂ is added, the situation is considered first where monosulfate carbonates according to Eq. (3) and the generated monocarbonate does not react with CO₂. Owing to the molar ratio of monosulfate and CO₂ in Eq. (3), the amount of CO₂ is x/2 mol. The amount of CO₂ (*b* mol) can be expressed by that of gypsum as deducted in Eqs. (26) and (27).

$$\begin{cases} x + y = 1\\ 2y = a\\ b = x/2 \end{cases}$$
(26)

$$\begin{cases} x = 1 - a/2 \\ y = a/2 \\ b = 1/2 - a/4 \end{cases}$$
(27)

In the case of the carbonation of monocarbonate (Eq. (4)), it is worth noting that Eqs. (3) and (4) can be merged to Eq. (30) where the molar ratio of



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$$\begin{cases} x + y = 1\\ 2y = a\\ b - 2x \end{cases}$$
(28)

(28) and (29).

$$\begin{cases} x = 1 - a/2 \\ y = a/2 \\ b = 2 - a \end{cases}$$
(29)

$$3C_4 A \overline{S} H_{12} + 6 \overline{C} + 2H \rightarrow C_6 A \overline{S}_3 H_{32} + 6C \overline{C} + 2A H_3$$
(30)

Under the circumstance of complete carbonation of ettringite from Eq. (3), it can be concluded to Eq. (6) where the molar ratio of monosulfate and CO₂ is 1/3. Therefore, the amount of CO₂ is $3 \times \text{mol}$. In the same way, BIII can be expressed as 'b=3-3a/2', as deducted in Eqs. (31) and (32).

$$\begin{cases} x + y = 1\\ 2y = a\\ b = 3x \end{cases}$$
(31)

$$\begin{cases} x = 1 - a/2 \\ y = a/2 \\ b = 3 - 3a/2 \end{cases}$$
(32)

When ettringite begins to carbonate, the generated gypsum is likely to participate in the hydration reaction in Eq. (2). As a result, C_4A_3S in Eq. (2) will react with initial gypsum and later generated one, respectively. In consideration of this situation, the amount of the later gypsum is *x* mol for the ratio of C_4A_3S and gypsum in Eq. (2). According to Eq. (2), the amount of C_4A_3S reacting with later gypsum is *x*/2 mol. Equations can be obtained below.

$$\begin{cases} x + y + x/2 = 1\\ 2y = a\\ b = 3x \end{cases}$$
(33)



From Eq. (33), it can be seen that when taking the reaction of gypsum derived from carbonation products and C_4A_3S into account, BIII can be counted as an exceptional circumstance of BII (b=2-a).

When all of the phases carbonate entirely, the reactions can be included to Eq. (5) and Eq. (6). Different from BIII, ettringite in Eq. (5) originates from the hydration product in Eq. (2), and thus the generated monosulfate is x mol and ettringite is y mol. The total amount of CO_2 is 3 mol and it represents TB, as obtained in Eqs. (35) and (36).

$$x + y = 1$$

$$3x + 3y = b$$

$$2y = a$$
(35)

$$\begin{cases} x = 1 - a/2 \\ y = a/2 \\ b = 3 \end{cases}$$
(36)

Under the circumstance of gypsum formation, a small part of $C_4A_3\overline{S}$ is likely to react with it, which will make a difference to the amount of generated monosulfate and ettringite. If the number of (x+y)is less than 1, the generated gypsum from Eq. (5) and (6) will react with the unreacted $C_4A_3\overline{S}$. So the number of generated gypsum from Eq. (5) and (6) is set as (x+3y) mol. According to Eq. (2), the amount of $C_4A_3\overline{S}$ reacting with generated gypsum is (x+3y)/2 mol and (x+3y)/2 mol ettringite is formed. The consumed amount of CO_2 in Eq. (5) is (3x/2 + 15y/2) mol and the total amount of CO₂ can be expressed by 3x/2 + 15y/2 + 3x'. Hence the total $C_4A_3\overline{S}$ participating in the hydration is (3x/2+5y/2)mol. From Eq. (37), it can be seen that b equals to (9x/2 + 15y/2), which demonstrates that b constantly equals to 3 in spite of gypsum formation.

$$\begin{cases} 3x/2 + 5y/2 = 1\\ 3x/2 + 15y/2 + 3x = b \end{cases}$$
(37)

On the basis of above calculation and analysis, gypsum formation has no impact on the boundary establishment. Hence, analysis of zone will directly discuss occurrence of reaction and consumption of CO_2 in each zone irrespective of gypsum from carbonation products reaction with $C_4A_3\overline{S}$.

Zone

In Zone I, the amount of C_4A_3S participating in Eqs. (1) and (2) is also set as *x* mol and *y* mol, and that of CO_2 participating in Eq. (3) is set as *z* mol. According to the ratio of monosulfate and CO_2 in Eq. (3), the amount of CO_2 is *x*/2. The results in Eq. (39) indicates that the number of C_4A_3S participating in Eq. (1) and Eq. (2) is 2*b* mol and *a*/2 mol and *b* mol CO_2 will be consumed.

$$\begin{cases} x = 2z \\ 2y = a \\ z = b \end{cases}$$
(38)

$$\begin{cases} x = 2b \\ y = a/2 \\ z = b \end{cases}$$
(39)

In Zone II, monosulfate carbonates completely according to Eq. (3) and the generated monocarbonate reacts with CO₂ partially. The amount of C₄A₃ \overline{S} participating in Eq. (1) is set as *x* mol and that of CO₂ involved in Eq. (4) is set as *z* mol. As a consequence, *x*/2 mol monocarbonate is generated according to molar ratio of monosulfate and monocarbonte in Eq. (3). The results in Eq. (41) illustrate that the amount of CO₂ involved in Eq. (4) is (3*b*/4) mol and that of C₄A₃ \overline{S} in Eqs. (1) and (2) is (*b*/2) and (*a*/2) mol.

$$\begin{cases} x/2 + z = b \\ 2y = a \\ z = 3x/2 \end{cases}$$
(40)

$$\begin{cases} x = b/2\\ y = a/2\\ z = 3b/4 \end{cases}$$
(41)



In Zone III, when Eqs. (3) and (4) completely occur, it can be concluded to Eq. (30) with no formation of monocarbonte, an intermediate carbonation product of monosulfate. The amount of C_4A_3S participating in Eq. (1) is set as x mol and that of CO_2 in Eq. (5) is set as z mol. On the account of the ratio of monosulfate and CO_2 in Eq. (7), the consumed CO_2 in Eq. (13) is $2 \times \text{mol}$. The results in Eq. (43) represent that CO_2 partaking in Eq. (5) is (b/3) mol and the number of C_4A_3S participating in Eqs. (1) and (2) is (b/3) mol and (a/2) mol.

$$\begin{cases} 2x + z = b \\ 2y = a \\ z = x \end{cases}$$
(42)

$$\begin{cases} x = b/3 \\ y = a/2 \\ z = b/3 \end{cases}$$
(43)

In Zone IV, supposing that the amount of CO_2 participating in Eq. (5) is set as *z* mol. In the light of ratio of monosulfate and CO_2 in Eq. (6), the amount of CO_2 reacting with monosulfate is $3 \times \text{mol}$. The results in Eq. (45) illustrate that $(3a/2) \text{ mol} CO_2$ is consumed in Eq. (5) and the amount of C_4A_3S in Eqs. (1) and (2) is (b/3-a/2) and (a/2) mol, respectively.

$$\begin{cases} 3x + z = b \\ 2y = a \\ z = 3y \end{cases}$$
(44)

$$\begin{cases} x = b/3 - a/2 \\ y = a/2 \\ z = 3a/2 \end{cases}$$
(45)

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