ARTICLE IN PRESS

Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Influence of iron content on processing conditions and early age hydration of ye'elimite

Bipina Thaivalappil *, Piyush Chaunsali

Indian Institute of Technology Madras, Department of Civil Engineering, Chennai, India

ARTICLE INFO

Article history:
Available online xxxx

Keywords:
Calcium Sulfoaluminate-Belite cement
Iron content
Ye'elimite
Hydration

ABSTRACT

Ye'elimite is the primary reactive component in calcium sulfoaluminate-belite (CSAB) cement, and it has relatively lower raw material carbon footprint compared to Portland clinker phases. Ye'elimite produces ettringite when hydrated in the presence of calcium sulfate, and monosulfate in the absence of a sulfate source. The early age hydration properties in CSAB based binders are mainly controlled by the amount and reactivity of ye'elimite in the system. The reactivity of the ye'elimite can be affected by the presence of minor elements in raw mix during clinkering and distribution of other phases in the binder. This paper aims to study the formation and hydration o f ye'elimite incorporated with iron, which is commonly found in industrial by-products suitable for CSAB cement production. The influence of iron on the clinkering conditions and its incorporation in the ye'elimite phase are investigated using characterization techniques such as X-ray diffraction and thermogravimetric analysis. The iron-incorporated ye'elimite, synthesized using laboratory-grade chemicals, is examined for early-age hydration using isothermal calorimetry to study the effect of iron content on the hydration reactivity of ye'elimite. The iron content in the raw mix was found to affect clinkering reactions by accelerating the decomposition of calcite and calcium sulfate. The iron incorporation also resulted in changes in the crystal structure and early age hydration of ye'elimite.

Selection and peer-review under responsibility of the scientific committee of the 4th International Congress on Materials and Structural Stability.

1. Introduction

Calcium sulfoaluminate-belite (CSAB) cement is considered as a technically adequate low-CO_2 alternative binder to Portland cement (PC) for various applications [1,2]. Ye'elimite ($C_4A_3\hat{S}$ in cement chemistry notation, where C = CaO, A = Al_2O_3, $\hat{S}$ = SO_3) constitutes the major phase in CSAB cement along with belite and ferrite as the other main phases [3]. CSAB cement is primarily known for its high early-age strength development and shrinkage compensation properties. Both these properties are directly linked with the early age hydration, which is mainly dependent on the presence of ye'elimite phase. CSAB cement is produced using limestone, clay, bauxite, and calcium sulfate as raw materials. The use of bauxite as a major source for the high fraction of alumina in CSAB cement increases its manufacturing cost significantly. In recent years, the utilization of various industrial by-products as alternative raw materials to produce CSAB cement is being promoted for its economic and environmental advantages. Alumina rich by-products or waste-materials such as red mud, low-grade bauxite, and aluminum anodizing sludge are potential alternatives for bauxite in CSAB cement production. However, when alternative raw materials are used, certain trace elements or impurities are unavoidably present in the raw mix, which can influence the processing conditions as well as performance of the cement. Iron is unavoidably present in the CSAB raw mix as most of the natural materials used for CSAB cement manufacturing contain a considerable amount of iron. As the high-alumina bearing raw materials are expensive and scarce, iron-bearing low-alumina sources like red mud and low-grade bauxite are gaining more research interest as potential raw material alternatives for CSAB cement. The high-iron bearing CSAB cements are also referred to as iron-rich or ferric-rich calcium sulfoaluminate (IR-CSA or FR-CSA) cement [4,5]. Along with promoting the recycling of Fe, Al - containing industrial solid wastes, the incorporation of iron in CSAB cement can help to accelerate the clinkering process by acting as a flux.

The iron content in raw mix can be in solid-solution with ye'elimite ($C_4A_{3-x}F_x\hat{S}$, where F = Fe_2O_3) and belite, and it also forms

---

* Corresponding author.

E-mail address: ce20d700@smail.iitm.ac.in (B. Thaivalappil).

https://doi.org/10.1016/j.matpr.2023.07.004
2214-7853/
Selection and peer-review under responsibility of the scientific committee of the 4th International Congress on Materials and Structural Stability.

Please cite this article as: B. Thaivalappil and P. Chaunsali, Influence of iron content on processing conditions and early age hydration of ye'elimite, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2023.07.004

iron-bearing phases such as C_4AF, C_2F, and CF [4]. In order to reduce the demand for high-alumina bearing materials in the raw mix and optimize the clinkering conditions, it is necessary to understand the controlling factors for the formation of iron-bearing phases. Although a few studies [6–9] have attempted to understand the extent of substitution of iron in CSAB phases, the existing results are inconsistent. A previous study reported maximum incorporation of Fe_2O_3 in $C_4A_{3\text{-}x}F_x\hat{S}$ as x = 0.32 and the incorporation level depends on ratio between Fe_2O_3 and Al_2O_3 of the raw mix [6]. The maximum level of substitution was found to be closely similar (x = 0.33) in another study [5]; however, the incorporation level was highly affected by the $CaSO_4$ content. Various other works have reported values for 'x' varying between 0.08 and 1.20 [7–9]. The broad range of values for maximum substitution levels of iron and contradictory results on factors affecting the formation of different phases in different clinkering conditions emphasize the need for further study. This work focuses on understanding the influence of iron substitution in the raw meal on the formation and reactivity of ye'elimite. As the early age hydration in CSAB based binders is mostly based on the hydration of ye'elimite, only ye'elimite phase is considered for the study.

2. Materials and methodology

2.1. Laboratory synthesis of ye'elimite

Pure ye'elimite was synthesized in laboratory scale using reagent grade calcium oxide (CaO), alumina (Al_2O_3), and calcium sulfate anhydrite ($CaSO_4$). However, for the thermogravimetry investigation on rawmix, $CaCO_3$ was used instead of CaO in order to capture decomposition of $CaCO_3$. For iron incorporation in the raw mix, reagent grade Fe_2O_3 was used. All the materials used are of purity > 95%. The steps involved in the synthesis process are detailed below.

Step 1 — Proportioning of raw materials: The stoichiometric proportion of the oxides were calculated for pure ye'elimite. As the volatilization of sulfur may happen beyond 1200 °C, but the ye'elimite formation would continue above this temperature, an additional 5% of $CaSO_4$ was added to the raw mix to compensate the loss of sulfur and ensure maximum yield of ye'elimite during clinkering.

Step 2 — Mixing of raw materials and pelletization: In this step, the proportioned raw mix was homogenized by adding water followed by mixing using a stirrer. The raw mix was kept in an oven at 100 °C for 12 h to remove the water. Further, the mix was pelletized under 1.5 ton in a Controls – 250 kN servo hydraulic - compression testing machine for facilitating the solid-state reactions during clinkering process.

Step 3 — Sintering and cooling: The raw mix pellets were placed in alumina crucibles and fired in an electric muffle furnace at a heating rate of 5 °C/min. A maximum temperature of 1400 °C and a retention time of 1 h were used for the synthesis. A clinkering temperature higher than the commercial CSAB clinkering temperature (1250–1300 °C) was used inorder to ensure maximum yield of pure ye'elimite and avoid formation of minor phases. The clinkers were further cooled down to room temperature.

Step 4 — Grinding: The clinker, after cooling, was taken for grinding in a planetary ball mill. All clinkers were ground to a similar fineness (D_{50} = 45–50 μm).

2.2. Characterization

The clinkers were wet ground using an agate mortar and pestle with isopropanol as grinding media to pass through 75 μm sieve for the X-ray diffraction (XRD). Hydration study was conducted on paste samples hydrated with a water to binder ratio of 0.6. Hydrated samples were taken for XRD after hydration stoppage using isopropanol followed by the same micronizing process. It was ensured that the entire quantity taken for grinding was passed through the 75 μm sieve in order to avoid fractionation of the samples. The phase assemblage of the synthesized clinkers and hydrated cements were determined using the X-ray diffractogram obtained from Rigaku X-ray diffractometer equipped with Cu-Kα radiation tube (λ = 1.5408 Å). The 2θ was varied from 5 to 60° with 0.01° step size. The quantitative phase analysis was carried out using Rietveld refinement using PANalytical Xpert High Score Plus Software V.3. For quantifying amorphous phases in hydrated samples, internal standard method was used. Reagent grade ZnO (>99% purity) was used as the internal standard at a doping level of 20% by mass. Table 1 shows the collection codes used for identifying the mineralogical phases during XRD analysis.

Thermogravimetric analysis (TGA) was carried out using LABSYS evo TG-DTA/DSC-1600 °C model equipment on selected raw mixes. The TGA was performed at a heating rate of 10 °C/min under N_2 atmosphere.

Hydration kinetics of the ye'elimite samples were studied using calorimetry. Calmetrix I-Cal HPC isothermal calorimeter with four sample channels was used to measure the heat evolution during the hydration of ye'elimite. Paste samples were mixed for 3 min and placed inside the calorimeter in respective channels.

3. Results and discussion

3.1. Clinkering and formation of phases

The proportion of the raw mixes and processing parameters used for synthesis are shown in Table 2. The XRD pattern (Fig. 1) shows the presence of anhydrite peak in pure ye'elimite mix whereas it was almost disappeared in the iron-incorporated ye'elimite, indicating that iron has facilitated reaction of calcium sulfate during clinkering. The phase assemblages of the synthesized ye'elimite were quantified using Rietveld refinement (Table 3). The total ye'elimite yield was reduced in the 5F and 10F due to the substitution of iron in the ye'elimite raw mix compared to the pure ye'elimite (Y). The iron content in raw meal facilitated the formation of more cubic ye'elimite at the expense of orthorhombic ye'elimite. Some part of the iron went into the ye'elimite structure and stabilized its cubic polymorph, while some

Table 1
Phases and collection codes used for quantitative XRD analysis using Rietveld refinement.

Phase Name	Notation used for labelling in XRD pattern	Cement chemistry notation	Collection code
Ye'elimite 80361 (ICSD)	(Orthorhombic)	Y	$C_4A_3\check{S}$-o
Ye'elimite (Cubic)	Y	$C_4A_3\check{S}$-c	9560 (ICSD)
Calcium sulfate Anhydrite	A	$C\check{S}$	15876 (ICSD)
Brownmillerite	B	C_4AF	98830 (ICSD)
Dicalcium Ferrite	F'	C_2F	27111 (ICSD)
Ettringite	E	AFt	155395 (ICSD)
Gypsum	G	$C\check{S}H_2$	409581 (ICSD)
Internal standard			
Zincite	Z	Z	9008877 (COD)

Table 2
Raw mix proportion and clinkering parameters for ye'elimite synthesis.

Sample ID	Ye'elimite (wt%)	Fe_2O_3 (wt%)	Maximum Clinkering temperature (°C)	Retention time (h)
Y	100	0	1400	1
5F	95	5	1400	1
10F	90	10	1400	1

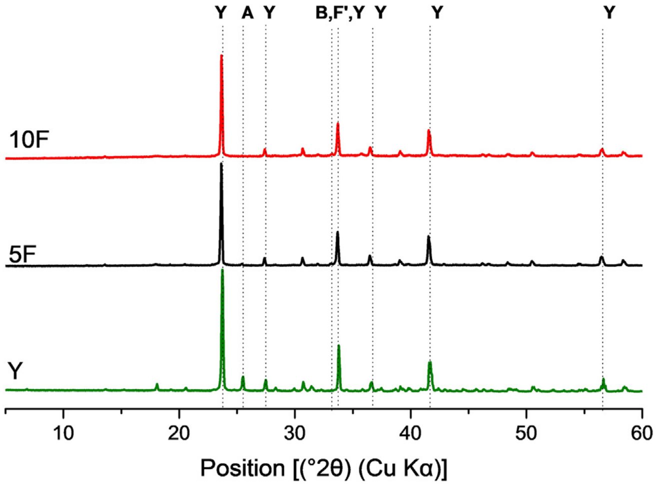

Fig. 1. X-ray diffractogram of synthesized ye'elimite with varying iron incorporation.

part of iron contributed to the formation of ferrite phases like C_4AF and C_2F [6–8].

The effect of iron content on ye'elimite formation was also investigated using TGA. As iron incorporation of up to 10% in the ye'elimite raw mix did not have a significant influence on the sintering, effect of a higher level of iron content (20%) is studied. The decarbonation of $CaCO_3$ and decomposition of $CaSO_4$ were influenced in the presence of 20% iron as shown in the TGA curve in Fig. 2. The decarbonation and sulfur evaporation occur at a relatively lower temperatures in the iron incorporated raw mix compared to the pure ye'elimite raw mix [4,10].

3.2. Hydration reactions and kinetics

The hydrate phase evolution of the pure and iron-incorporated ye'elimite was investigated at the ages of one day and three days using XRD (Fig. 3). A water to binder ratio (w/b) of 0.6 and molar ratio of gypsum to ye'elimite (M value) of 2 were used in all the mixtures. The main hydration product was ettringite and the amount of ettringite quantified using Rietveld method is shown

Table 3
Clinker phases quantified using Rietveld refinement.

Sample ID	$C_4A_3\check{S}$-o	$C_4A_3\check{S}$-c	$C\check{S}$	C_4AF	C_2F
Y	91.0	0.7	7.2	0	0
5F	64.1	21.0	1.6	7.3	6.0
10F	60.7	22.8	0	9.2	7.4

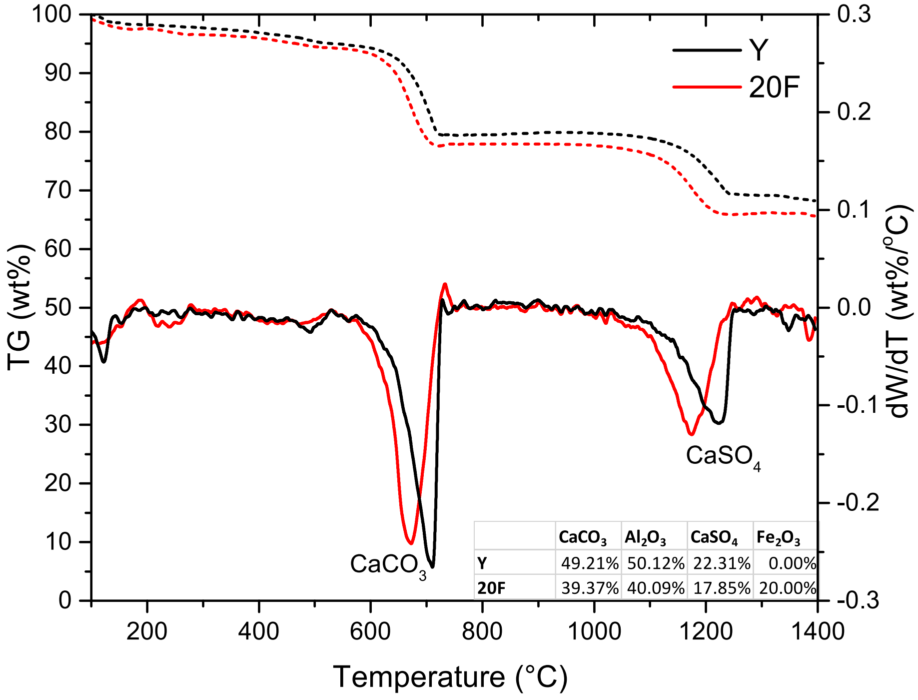

Fig. 2. Thermogravimetry curve for pure ye'elimite raw mix (black) and raw mix containing iron (red) *(Note: TG curve in dashed line and dW/dT curve in solid line).* (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

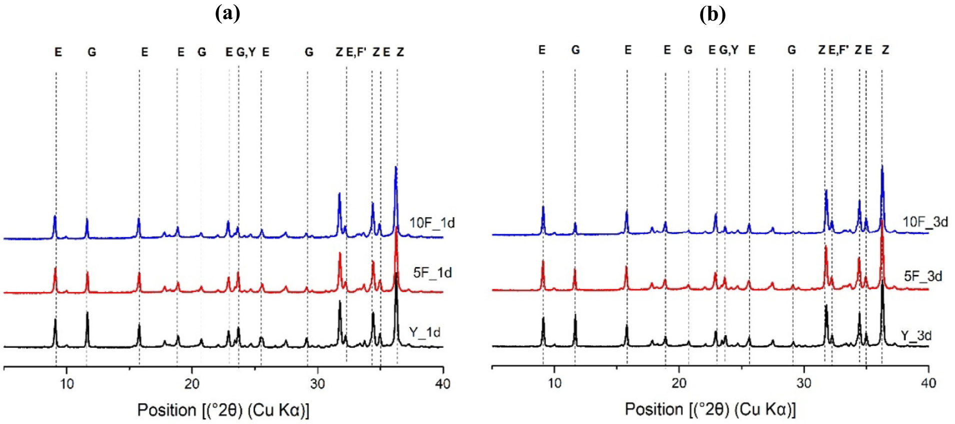

Fig. 3. X-ray diffractogram of 1-day (a) and 3-day (b) hydrated ye'elimite with varying iron incorporation.

in Fig. 4. The ettringite amount is comparable in all the samples at both the ages. In the pure ye'elimite mix, there was no significant increase in the amount of ettringite from one day to three days, indicating that the ye'elimite hydration doesn't progress significantly beyond one day. However, in the iron containing mix, hydration progresses by a comparatively higher degree as indicated by the increase in amount of ettringite. The incorporation of iron up to 10% have slightly increased the ettringite at the end of 3-day hydration.

Fig. 5 shows the heat flow calorimetry of the ye'elimite with gypsum mixtures examined. It can be clearly seen from the heat rate curves that the iron-containing ye'elimite mixes (5F & 10F) behave differently compared to the pure ye'elimite mixture (Y). This can be attributed to the fact that the two modifications of ye'elimite – (orthorhombic and cubic) react differently during the early stages of hydration [4,11]. The dormant period is almost same (∼5h) in both the iron-containing ye'elimite whereas the dormant period is reduced in the pure ye'elimite, which is mostly composed of only orthorhombic ye'elimite. This is indicating that the initial dissolution of constituent phases (mainly ye'elimite in this case) is decelerated in the presence of iron at very early age and thus the formation of hydration products (ettringite). Similar results were reported by a previous study [4]. Also, two heat flow maxima are seen in the pure ye'elimite. In a prior study [11], the two peaks appeared for the orthorhombic and cubic polymorphs of ye'elimite were attributed to a two stage formation of ettringite. However, the iron-containing ye'elimite formed a more continuous heat flow, possibly indicating a continuous precipitation of ettringite rather than two stage phenomena. The cumulative heat flow curves depict the lower reaction turnover in the iron containing mixes in the early ages, especially in the initial 10–15 h. Beyond this period, there's no significant increase in the heat released in the pure ye'elimite mixture. However, the heat released in 5F and 10F mixes increased significantly and beyond 20 h, the total heat released were even slightly more than that of the pure ye'elimite mix. This is indicating that, though the early age hydration is slightly decelerated, the overall hydration by three days is not significantly influenced by the presence of iron content in ye'elimite or other iron-containing phases in the system.

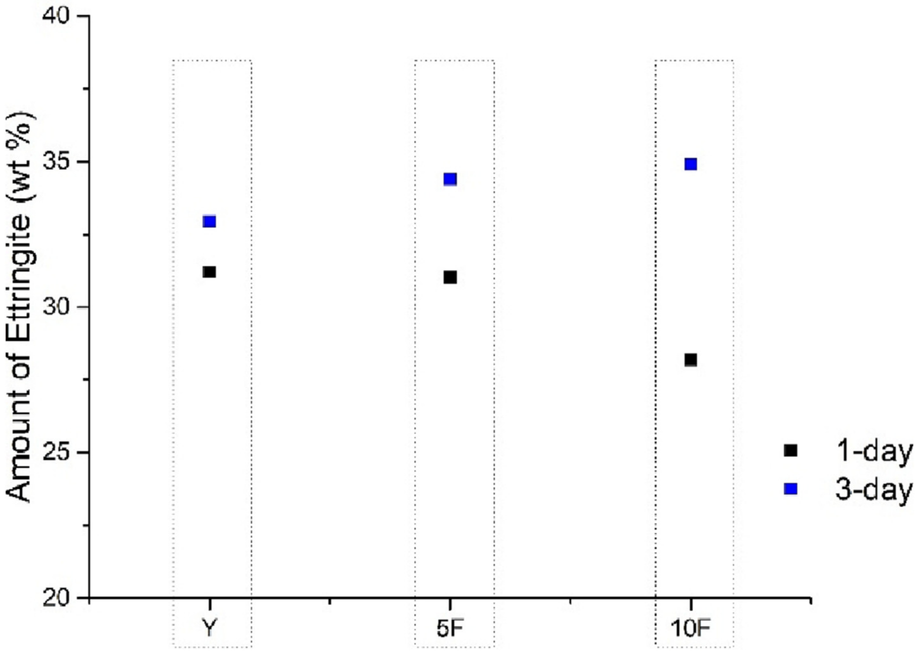

Fig. 4. Amount of Ettringite formed in 1-day and 3-day hydrated ye'elimite with varying iron incorporation.

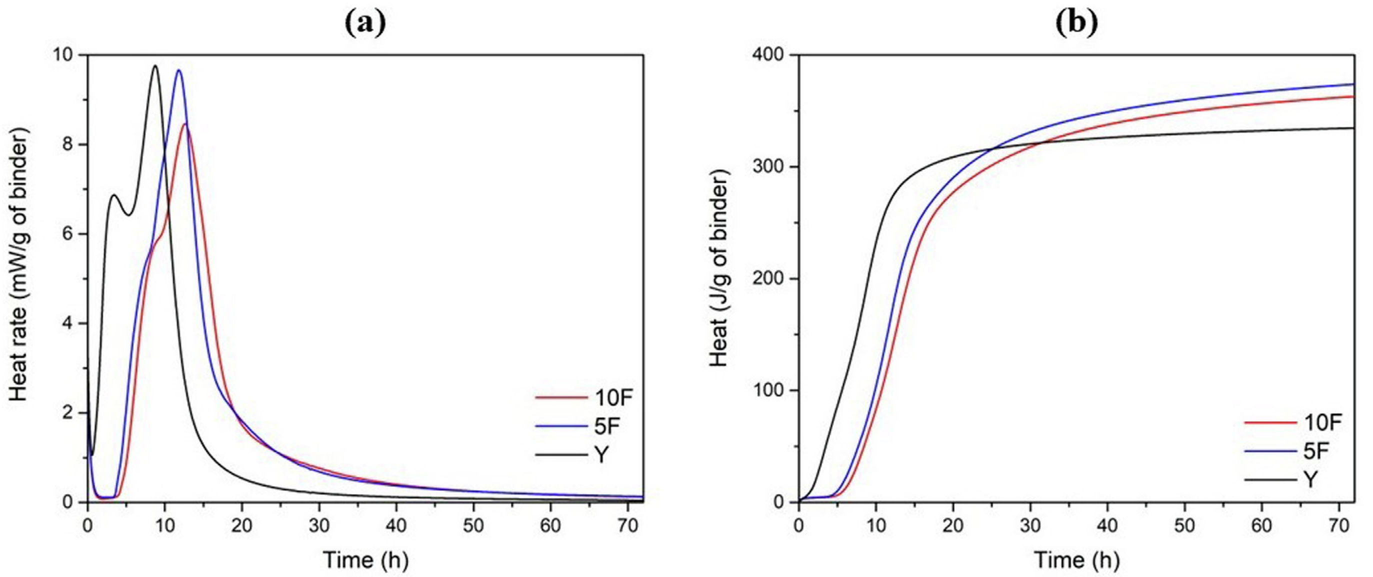

Fig. 5. Isothermal calorimetry of ye'elimite synthesized with varying amount of iron content, in presence of gypsum (w/b = 0.6) a) Heat flow b) Cumulative heat released.

4. Conclusions

The present work focused on investigating the effect of incorporation of iron in the raw mix on the synthesis and hydration of ye'elimite. The presence of iron is unavoidable when industrial by-products/residues like red mud is used for CSAB clinker production. It was found that iron content could accelerate the decomposition of $CaCO_3$ and $CaSO_4$. Hence the clinkering conditions need to be chosen carefully when there's iron present in the raw mix. While some part of the iron in the raw meal is going into the ye'elimite structure, replacing Al^{3+}, some part is forming ferrite phases with calcium and aluminum. The iron content stabilized more cubic ye'elimite at the expense of the orthorhombic ye'elimite, which is generally found in the commercial CSAB clinker. In order to investigate the effect of change in phase distribution in the clinker as well as the change in crystal structure of ye'elimite due to the presence of iron, the early age hydration of iron-containing ye'elimite was compared against stoichiometric ye'elimite. The iron content slightly decelerated the very early age (initial 10–15 h) hydration, but the 3-day hydration was comparable to that of the stoichiometric ye'elimite. Up to 10% of iron incorporation in ye'elimite raw meal resulted even a slightly higher cumulative heat; hence more reaction turnover at the end of three days. To have a comprehensive understanding of the influence of iron content on ye'elimite hydration, its role on dissolution of constituent phases and microstructure development are currently being investigated.

CRediT authorship contribution statement

Bipina Thaivalappil: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Piyush Chaunsali:** Conceptualisation, Methodology, Validation, Visualisation, Writing – review and editing.

Data availability

Data will be made available on request.

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.

Acknowledgements

The first author would like to thank Ministry of Education of India for the Prime Minister's Research Fellowship (PMRF). The authors wish to acknowledge the experimental facilities provided by the Department of Civil Engineering, IIT Madras. The Institute of Eminence Research Initiative grant on Technologies for Low Carbon and Lean Construction from IIT Madras is gratefully acknowledged.

References

[1] E. Gartner, Industrially interesting approaches to ”low-CO2 ” cements, Cem. Concr. Res. 2004; 1489–1498 Industrially. https://doi.org/10.1016/j.cemconres.2004.01.021.

[2] Piyush Chaunsali, S. Vaishnav Kumar, Calcium sulfoaluminate-belite cements: opportunities and challenges, Indian Concr. J. (2020).

[3] L. Zhang, M. Su, Y. Wang, Development of the use of sulfo- and ferroaluminate cements in China, Adv. Cem. Res. (1999) 15–21, https://doi.org/10.1680/adcr.1999.11.1.15.

[4] Y. Huang, Y. Pei, J. Qian, X. Gao, J. Liang, G. Duan, P. Zhao, L. Lu, X. Cheng, Bauxite free iron rich calcium sulfoaluminate cement: Preparation, hydration and properties, Constr. Build. Mater. (2020), https://doi.org/10.1016/j.conbuildmat.2020.118774.

[5] X. Yao, S. Yang, Y. Huang, S. Wu, Y. Yao, W. Wang, Effect of $CaSO_4$ batching in raw material on the iron-bearing mineral transition of ferric-rich sulfoaluminate cement, Constr. Build. Mater. (2020), https://doi.org/10.1016/j.conbuildmat.2020.118783.

[6] F. Bullerjahn, T. Scholten, K.L. Scrivener, M. Ben Haha, A. Wolter, Formation, composition and stability of ye'elimite and iron-bearing solid solutions, Cem. Concr. Res. (2020).

[7] D. Chen, X. Feng, S. Long, The influence of ferric oxide on the properties of $3CaO \cdot 3Al_2O_3 \cdot SrSO_4$, Thermochim. Acta. (1993) 143–155, https://doi.org/10.1016/0040-6031(93)80088-R.

[8] F. Bullerjahn, D. Schmitt, M. Ben Haha, Effect of raw mix design and of clinkering process on the formation and mineralogical composition of (ternesite) belite calcium sulphoaluminate ferrite clinker, Cem. Concr. Res. (2014) 87–95, https://doi.org/10.1016/j.cemconres.2014.02.004.

[9] F.Z. Abir, M. Mesnaoui, Y. Abouliatim, L. Nibou, T. Labbilta, Y. El Hafiane, A. Smith, Effect of the addition of iron oxide on the microstructure of ye'elimite, Cem. Concr. Res. (2022), https://doi.org/10.1016/j.cemconres.2021.106625.

[10] B. Touzo, K.L. Scrivener, F.P. Glasser, Phase compositions and equilibria in the $CaO-Al_2O_3-Fe_2O_3-SO_3$ system, for assemblages containing ye'elimite and ferrite $Ca_2(Al, Fe)O_5$, Cem. Concr. Res. (2013) 77–86, https://doi.org/10.1016/j.cemconres.2013.08.005.

[11] D. Jansen, A. Spies, J. Neubauer, D. Ectors, F. Goetz-Neunhoeffer, Studies on the early hydration of two modifications of ye'elimite with gypsum, Cem. Concr. Res (2016), https://doi.org/10.1016/j.cemconres.2016.11.009.