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Synthesis of α'Dicalcium Silicate (C_2S) under an SO_2-Containing Atmosphere

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ABSTRACT

Mitigating greenhouse gas emissions is one of the main approaches to tackle the current environmental crisis. The decarbonation of the cement industry could significantly lower anthropogenic carbon emissions by limiting the average temperature rise to 2°C. Alternative cement formulations such as calcium sulfoaluminate (C$A) have great potential in partly replacing the current families of cement due to their lower carbon footprint, rapid strength gain, fast curing time, and lower shrinkage. The eco-friendly characteristics of C$A cement are attributed to reduced amounts of limestone used for production and lower synthesis temperatures. The challenge facing the production of C$A cement is mainly its requirement of high amounts of alumina which hinders the economic viability at the commercial scale. Alumina is essential for the formation of the ye'elimite phase which heavily contributes to early-age strength development. A promising technique to improve the process' economics is to reduce the alumina content requirement while preserving the early-age strength. This can be achieved by stabilizing the high temperature α' polymorphs of dicalcium silicate to ambient conditions. A technique was previously developed wherein elemental sulfur is utilized as a source of fuel and mineralogical control factor that provides the sulfur oxide needed to both preserve α' dicalcium silicate and form ye'elimite in the clinker. Synthesis of α'C_2S was carried out here with a focus on Na, K, B, and P as additives under a sulfur-containing atmosphere. The results display the successful stabilization of about 80% α'C_2S upon quantification. Hydration experiments showed that the isothermal heat release of α'C_2S deviates significantly from beta-C_2S. Highest degree of hydration was achieved with the boron stabilized α'C_2S. Interestingly after 6 days of hydration both investigated α'C_2S showed no portlandite formation but only calcium silicate hydrates (C-S-H).

KEYWORDS: *calcium sulfoaluminate (C$A), ye'elimite, alpha prime belite, low carbon cement, SEM-EDX-EBSD*

1. Introduction

Approximately 8% of global carbon dioxide emissions are emitted during the production of cement (Pearce, 2021). Various techniques, such as the utilization of alternative fuels and alternative cement formulations, have been explored to decrease these emissions. Calcium sulfoaluminate (C$A) cements are ye'elimite rich formulations that are produced at low temperatures and provide a reduction of raw material derived carbon emissions up to 35%-40% (Tao et al. 2023). However, the economic viability of these formulations suffers due to the increased Al_2O_3 content required in its raw mix designs. Replacing a portion of the raw mix Al_2O_3 with SiO_2 (at conventional C$A production temperatures) leads to a product with increased belite (C_2S) content and a consequently reduced early age strength. Reported studies have shown that the stabilization of high temperature polymorphs of dicalcium silicate could serve as a strategy to compensate for the aforementioned loss in mechanical performance. The alpha prime (α') group of polymorphs are highly reactive when hydrated and are considered to be the most effective hydraulic forms of C_2S when preserved under normal conditions. Cuesta et al. reported the stabilization of $\alpha' C_2S$ through doping mechanism of B and Na/B. When boron was added, a tetrahedral borate anion replaced silicon, while a triangular planar anion replaced silicon in the case of sodium/boron doping, resulting in a new stabilized α'-C_2S structure with ratios of α'-$Ca_{1.85}Na_{0.15}(SiO_4)_{0.85}(BO3)_{0.15}$ (Cuesta et al. 2012).

In a recently developed clinker production technique, a C$A cement was produced via the combustion of sulfurous fuels (Galan et al. 2017; Al Horr 2017) to provide both the sulfate precursor (via gas-solid sequestration) and a contribution towards heat needed for the C$A cement production process. Elhoweris et al. investigated the effect of this technique on the preservation of α' dicalcium silicate in C$A clinker at laboratory scale. The study demonstrated that, when using an SO_2 containing atmosphere and alkali dopants, α' C_2S containing C$A clinkers could be effectively preserved to ambient conditions by air cooled quenching (Elhoweris, 2020).

2. Methodology

2.1 C_2S Synthesis

Various batches of C_2S, synthesised using stoichiometric amounts of calcium carbonate ($CaCO_3$, Sigma Aldrich) and silicon dioxide (SiO_2, Sigma Aldrich), were prepared by incorporating potassium carbonate (K_2CO_3, Sigma Aldrich) and sodium carbonate (Na_2CO_3, Sigma Aldrich) i.e., K and Na as alkali additives and sodium tetraborate decahydrate ($Na_2[B_4O_5(OH)_4] \cdot 8H_2O$) and calcium phosphate ($Ca_3(PO_4)_2$) i.e. B and P with concentration ranging from (1 wt.% to 4 wt.%). Results shown here for samples PNa44 and BK11 (numbers indicate weight percentage of doping agent, i.e., PNa 44 is a C_2S synthesised with 4 wt.-% P and 4 wt.-% Na respectively). The C_2S were fired at 1300°C for 5 hrs under SO_2 containing conditions in a bottom loading furnace with gas mixture %vol of 0.62, 77.44, and 21.94 for SO_2, nitrogen and air respectively followed by a rapid cooling step. Hydration experiments are compared with standard beta-C_2S (obtained from Vush, Czech Republic). All samples were ground to a similar specific surface area (approximately 500 m^2/kg ± 20 m^2/kg)

2.4 Characterization of synthesized C_2S and hydration experiments

Isothermal heat release of C_2S was measured over a period of 142 h at w/c of 0.5. Hydration was stopped by immersing samples in isopropanol for 2h. For SEM analysis, samples were embedded in epoxy resins and polished according to standard protocols. SEM and back scattered electron (BSE) imaging combined with energy dispersive X-Ray spectroscopy (EDX) investigations were carried out in high vacuum. For XRD, the samples were ground, and measurements were performed using Cu radiation. Some of the XRD sample were also heated from room temperature to 1000°C and measured for heat flow and weight loss.

3. Results and Discussions

3.1 Characterization of Synthesized Clinkers

Amongst all the synthesised samples of different binary additive combinations, the BK11 and PNa44 showed the highest percentages of α' C_2S preservation within the clinker sample, e.g., about 80% and 75% respectively as determined by XRD-Rietveld analysis. Other silicates phases that were present included beta C_2S, NCS and C_3S_2.

3.2 Hydration of the synthesized clinkers

Results in Figure 1 show the heat flow of the selected C_2S hydrated using w/c of 0.5 during the first 142 hrs. The beta-C_2S shows the typical heat release curve, characterised by an induction, acceleration, and deceleration period. BK11 and PNa44 samples show two main hydration peaks, whereby for the BK11, first hydration maximum occurs at the earliest stage and the second maximum is most pronounced. The highest total heat observed, after 140 h of hydration, was that of sample BK11 at 64.38 J/g.

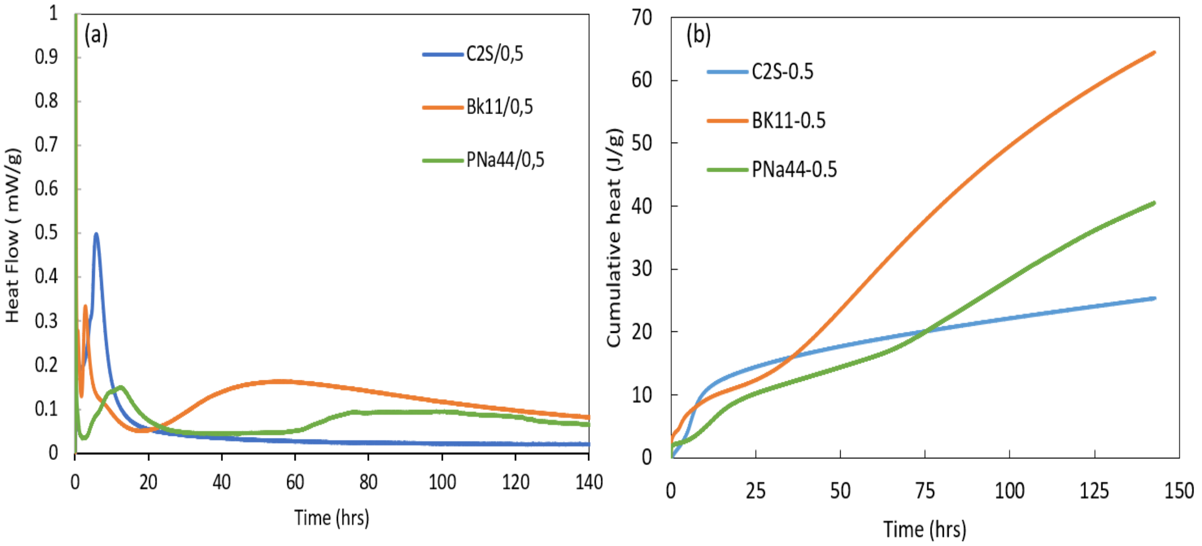

Figure 1: a) Isothermal heat release rate and b) cumulative heat release of C_2S pastes (w/c 0.50). For comparison purposes, pure beta-C_2S was used as a reference.

The microstructure of 6-days hydrated samples were evaluated by BSE imaging and EDX mapping analysis as shown in Figure 2. Results show that, after six days of hydration, the anhydrous material were predominately present, with only a minor amount of hydration products observed. Surprisingly, hardly any portlandite was identified, by BSE images and EDX mapping data, in BK11 and PNa44. Only the beta C_2S could be observed to have the common phase assemblage of hydrated belite, which is portlandite and C-S-H. The amount and thickness of C-S-H phases is largest in BK11 compared to PNa44 and beta-C_2S. The fewest amount of hydrates was seen in PNa44, which, after 6 days, was in a weakly solidified state. To confirm findings from the SEM-EDX analyses, DTA/TG analysis of 6 day hydrated clinkers were performed, with the corresponding mass loss data presented in Figure 2. The results confirmed that in PNa44 and BK11 no portlandite had formed. The total mass loss after 6 days of hydration is highest for BK11 (11.99 %) and lowest for beta C_2S (4.47 %), i.e., confirming SEM results.

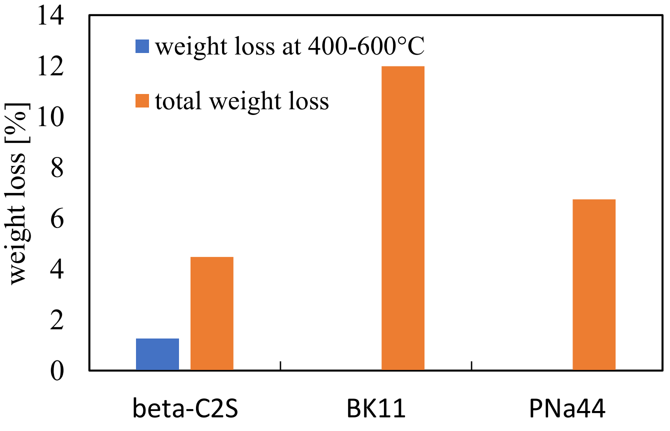

Figure 2: Weight loss (TG) after of 6 days hydration.

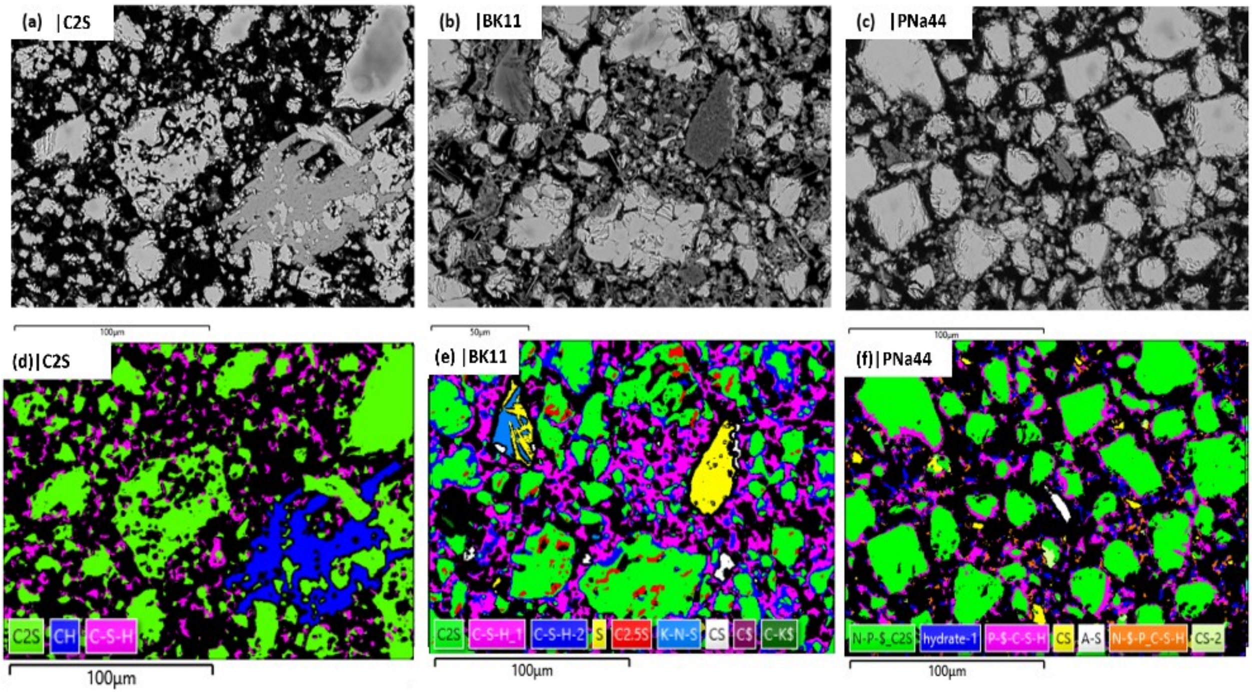

Figure 3: SEM-BSE images (a, b, c) and phase maps (d, e, f) derived from EDX analysis of 6 days hydrated C_2S, a/d) beta-C_2S, b/e) BK11 and c/f) PNa44, black color= epoxy/pores.

4. Conclusions

In conclusion, alpha prime C_2S was successfully synthesized at low temperature with the aid of alkali, boron and phosphorous based additives, rapid cooling and SO_2 containing atmosphere. The hydration studies also revealed that, the heat release of alpha prime C_2S differs significantly from regular beta-C_2S in that the main hydration is split into two peaks. This might have been caused by the fact that the samples contain alpha C_2S but also beta C_2S and some rankinite, more investigations are needed. After 6 days hydration, the boron - potassium stabilised C_2S showed the highest degree of reaction compared to beta-C_2S and the PNa44 sample. In both alpha prime C_2S containing samples, no portlandite formed after 6 days of hydration, if the reason for this is the stabilisation under SO_2 atmosphere will be revealed during further studies with samples synthesis at ambient conditions.

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