# Effects of Gypsum and Limestone on Early-Age Hydration and Strength Optimization in Belite Calcium Sulfoaluminate Cement

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## *1.0 Results and Discussion*

### *1.1. Thermogravimetric Analysis*

TGA analysis for binders at l/s 0.5 after 3-days of hydration were shown in **Figure S1**. In **Figure S1**, three mass loss zones have been identified at different temperatures. A significant mass loss peak around 120 °C, observed for all binders, corresponds to the presence of ettringite and C-S-H, consistent with prior studies[1,2]. At 150°C, a small hump can be observed which is attributed to the presence of C$\$H_2$ [3]. Similarly, the straetlingite and $AH_3$ (added to the remanent of ettringite) loses bonded water between 200°C and 300°C[1]. Between 700°C and 850°C the presence of C$\overline{C}$ can be observed[1,4].

**Figure S1(a)** showcases the mass loss profiles for M(2.99) binders at different C$\overline{C}$ replacement levels. In **Figure S1(a)**, the most notable observation is that the mass loss peak for ettringite is higher for M(2.99)_10% C$\overline{C}$, followed by other replacement levels (20 and 30% C$\overline{C}$). Another interesting observation is that the mass loss peak in plain CSAB is less than that of 10 and 20% C$\overline{C}$ binders. This clearly indicates the effect of water content on the hydration of precursors. At 150 °C the mass loss peak corresponding to C$\$H_2$ was almost insignificant but small variation can be seen indicating higher presence of C$\$H_2$ in 10% C$\overline{C}$ binder, followed by 20 and 30% C$\overline{C}$ binders. These observations of ettringite and C$\$H_2$ presence in the binders agree with XRD patterns shown in **Figure 2(b)**. Whereas the calcite weight loss peaks follow the similar trend as that of l/s 0.4. This concluded that the reactivity of limestone is limited but is enhancing the reactivity of ye'elimite with gypsum.

**Figure S1(b)** showcases the mass loss profiles for shows CSAB with 20% C$\overline{C}$ replacement at different M-ratios. In **Figure S1(b)**, it can be clearly seen that M(2.99) binder has higher mass loss associated to ettringite formation when compared to plain and other M-ratios. This is also in agreement with the XRD patterns shown in **Figure 3(b)**. At 150 °C the mass loss peak corresponding to C$\$H_2$ clearly shows the effect of M-ratio on the binders i.e., as the M-ratio increases the gypsum mass loss peak increases, similar to the profiles seen in **Figure 4 (b).** The calcite mass loss peaks follow the same trend as seen at l/s 0.4.

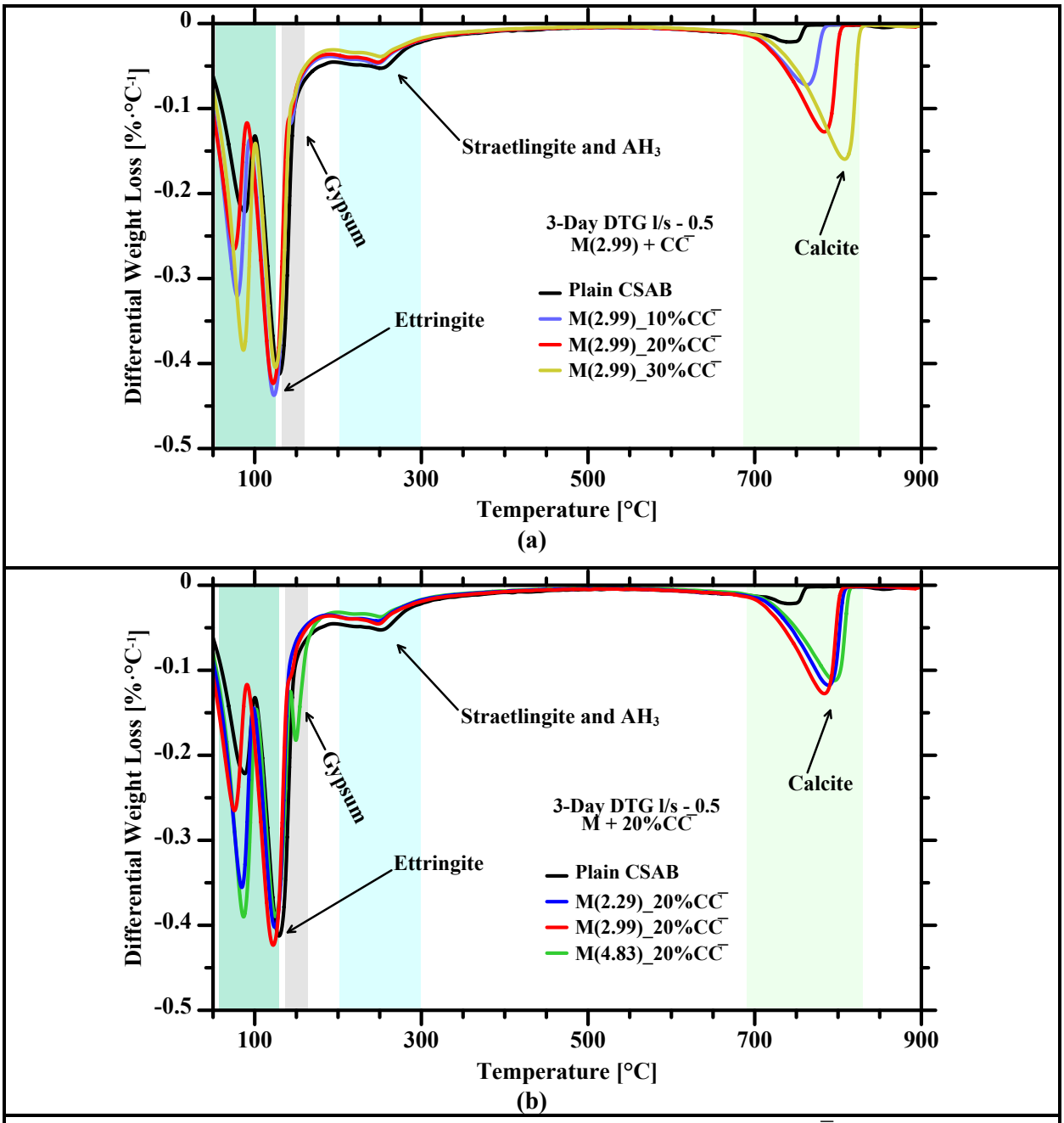


**Figure S1**. TGA profiles for l/s 0.5 at 3-days: **(a)** M(2.99) binders with three C$\bar{C}$ replacement levels; and **(b)** CSAB binders with 20% C$\bar{C}$ at three M-ratios.

As variations in respective mass loss peaks for C$H$$_2$ and C$\bar{C}$ content were observed in **Figure 4** and **Figure S1**, it is important to calculate their respective consumption amounts which will help in determining their reactivity. The relative reactivity of C$H$$_2$ and C$\bar{C}$ was shown in **Figure S2** by evaluating its initial

and final content in the binders, respectively. **Figure S2(a)** shows a linear trend between initial and final $C\overline{C}$ content at both l/s ratios, suggesting limited reactivity of $C\overline{C}$. The average reactivity of $C\overline{C}$ at l/s 0.4 is 0.70%, where as its reactivity at l/s 0.5 is 1.25% this agrees with both XRD and TGA figures shown in the manuscript. Similarly, in **Figure S2(b)**, the reactivity of $C\$H_2$ was determined. Here it can be observed that significant amount of $C\$H_2$ was consumed in plain CSAB at both l/s ratios resulting in slightly higher consumptions at higher water content (i.e., 91.3% at l/s 0.4 versus 94.2% at l/s 0.5). For blended binders, the amount of $C\$H_2$ consumption was found proportional (reactivity of ~83.60%) at both l/s ratios but with a small variation for 20% $C\overline{C}$ binder (reactivity of 65.2% at l/s 0.4, and 71.3% at l/s 0.5), indicating its noticeable dilution at higher water content. Consistent with previous sections, **Figure S2(b)** indicates that the water content in the binders allows for higher consumption of $C\$H_2$, with this effect being more pronounced in plain CSAB, 20%$C\overline{C}$ and 30%$C\overline{C}$ binders. This increased consumption could lead to additional ettringite formation. However, as the CSAB content decreases at higher levels of $C\overline{C}$ replacement, mechanical properties might not improve due to the presence of anhydrous phases. Thus, the microstructural evolution plays an important role in understanding the progression of the hydration of blended binders.

**Figure S2** concludes the importance of reactivity for both $C\$H_2$ and $C\overline{C}$ in these binders. The reactivity of $C\overline{C}$ in the blended binders is limited due to its polymorph form(i.e., calcite). Whereas the average reactivity of $C\$H_2$ is ~ 83.60% clearly implies the importance of its effect on the hydration.

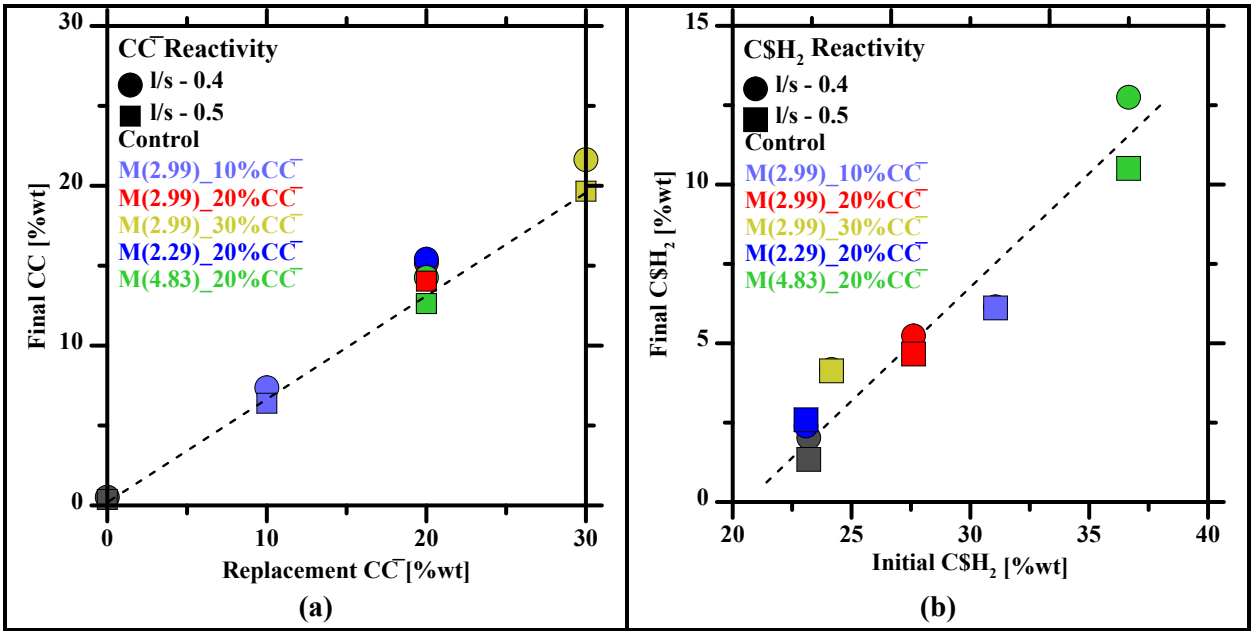


**Figure S2.** Reactivity calculation in selected CSAB binders at both the l/s ratios for: **(a)** C$\bar{C}$ with an average reactivity ~1.25%. And **(b)** C$H$$_2$ with an average reactivity ~83.60%.

### *1.2. Thermodynamic simulations*

Thermodynamic phase assemblages for selected binders at a l/s ratio of 0.5 are presented in **Figure S3**. **Figures S3 (a-b)** depict the phase assemblages of binders with a 20% C$\bar{C}$ replacement level at two distinct M-ratios. Similar to the phase assemblages observed in **Figures 5(d)** and **5(g)**, the hydrates formed are analogous; however, the increased water content at an l/s of 0.5 enhances the dissolution of C$H$$_2$, leading to a greater formation of ettringite. Consequently, the degree of hydration of CSAB increases at an l/s of 0.5 compared to the corresponding binders at an l/s of 0.4.

**Figures S3 (c-d)** illustrate the phase assemblages of M(2.99) binders at 10% and 30% C$\bar{C}$ replacement levels. At the 10% C$\bar{C}$ replacement level, the degree of hydration of CSAB is notably higher at an l/s of 0.5 compared to an l/s of 0.4. As the C$\bar{C}$ replacement level increases, the availability of water further enhances CSAB hydration. Additionally, binders at an l/s ratio of 0.5 exhibit increased porosity compared to those at an l/s of 0.4, attributed to the presence of excess water in the system.

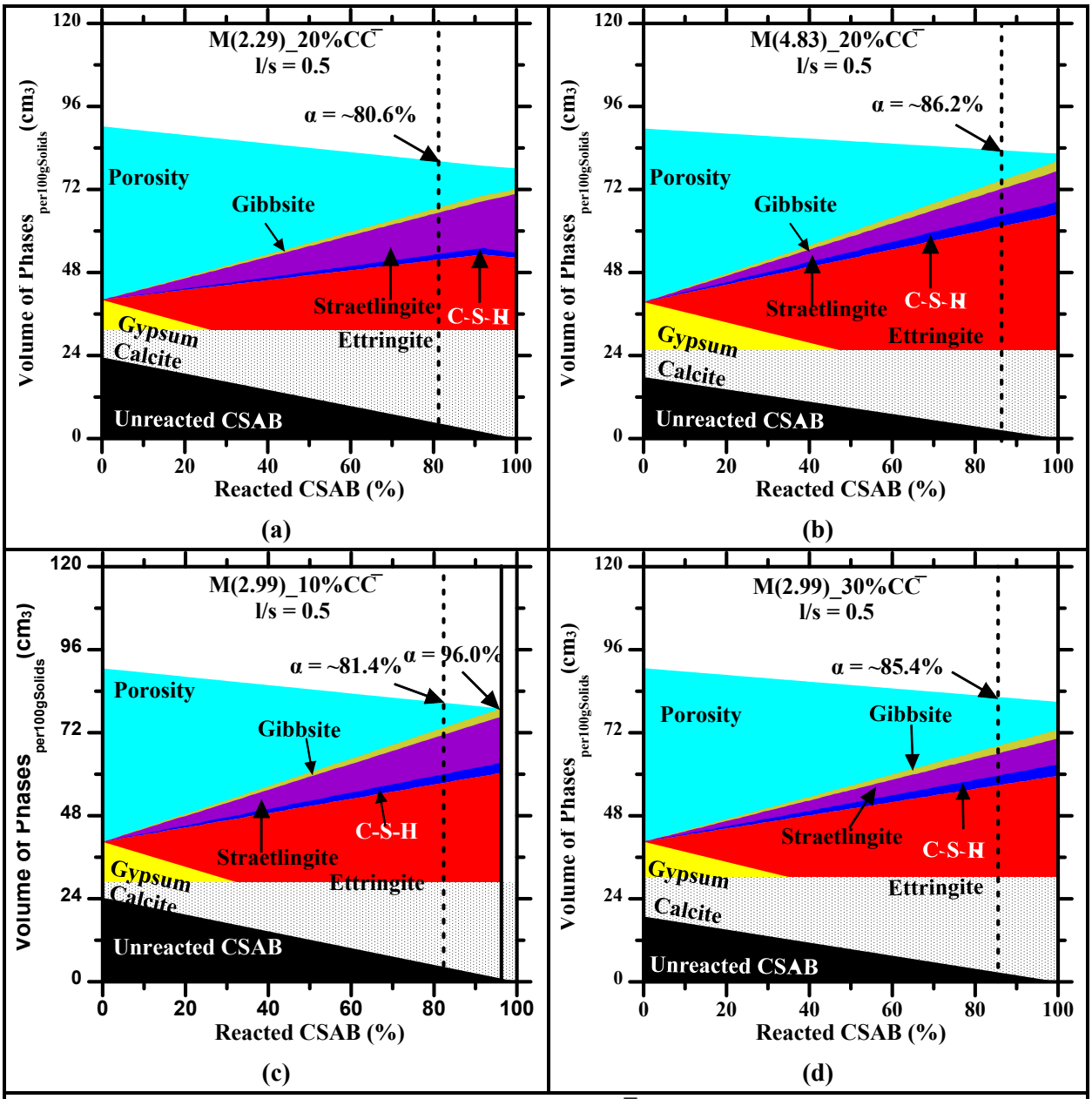


**Figure S3.** Thermodynamic phase assemblages of 20% C$\bar{C}$ binders at l/s of 0.5 with **(a)** 2.29 and **(b)** 4.83 M-ratios; M(2.99) binder at l/s of 0.5 with **(c)** 10% and **(d)** 30% C$\bar{C}$ replacement levels. The phase assemblages at 3 days are indicated with dashed line.

**Reference**


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