

Effect of dolomite powder on the hydration and properties of calcium sulfoaluminate cements made with different gypsum contents

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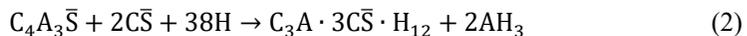
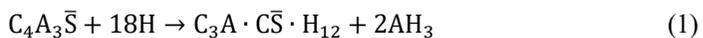
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INTRODUCTION

Dolomite $\text{CaMg}(\text{CO}_3)_2$ is an abundant carbonate mineral, and it frequently coexists with calcite in nature. Unlike limestone, dolomite is currently not accepted as a filler or component of cement because some forms of dolomite aggregates might cause concrete damage due to the dedolomitization. However, it has already been reported that the addition of dolomite in powder form to cement performs a comparable compressive strength to Portland-limestone cement [1,2]. Moreover, similar to limestone, dolomite may be involved in hydration of cement, resulting in the formation of carboaluminates and the stabilization of ettringite. Besides, Mg released from dolomite is considered to interact with the cement aluminates to form hydrotalcite, which leads to a decrease in the porosity and an increase in the compressive strength [3,4].

Calcium sulfoaluminate (CSA) cements is a type of cement consisting of the dominant mineral ye'elimite and has attracted extensive attention due to its low- CO_2 emission and energy-saving process [5]. Normally, about 15~25 wt% of calcium sulfate is interground with the clinker for optimizing setting time, strength development and dimension stability. The primary hydration products of CSA cement are crystalline monosulfate and ettringite as well as amorphous aluminum hydroxide (Eqs. 1 and 2). Based on the special hydration properties, CSA cement performs outstanding properties such as rapid-hardening, high early strength, shrinkage compensating, sulfate, and chloride corrosion resistance as well as immobilizing hazardous metals. Recently several studies have been published showing that limestone addition is beneficial to many properties of CSA cement, including enhancement of early-age hydration, stabilization of ettringite and improvement of strength loss at later age [6-8]. However, it is unclear whether the dolomite has a similarly positive effect on cement performance. Moreover, there is relatively little research on the use of dolomite in CSA cement.



In this study, the hydration and properties of CSA cement blended with dolomite at different M values (0, 1 and 2) were investigated. Similar mixtures containing limestone are prepared as a comparison. The phases were examined with X-ray diffraction and scanning electron microscopy.

EXPERIMENT

Commercial CSA clinker, dolomite, limestone, and analytical grade gypsum were used in this study. The chemical compositions determined by XRF are shown in Table 1. The dolomite and limestone powders contain 95.4% $\text{CaMg}(\text{CO}_3)_2$ and 95.5% CaCO_3 respectively, determined by TG analysis. The particle size distributions of the CSA clinker, dolomite and limestone determined by laser diffraction are given in Figure 1.

Table 1: Chemical and mineralogical composition of the used materials.

Material	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	LOI
Cement	65.35	18.14	4.28	2.93	0.60	2.90	0.80	0.10	2.96
Dolomite	31.21	0.89	0.22	0.10	21.78	0.01	0.05	-	45.67
Limestone	54.93	0.17	0.12	0.03	1.08	-	0.01	0.08	43.17

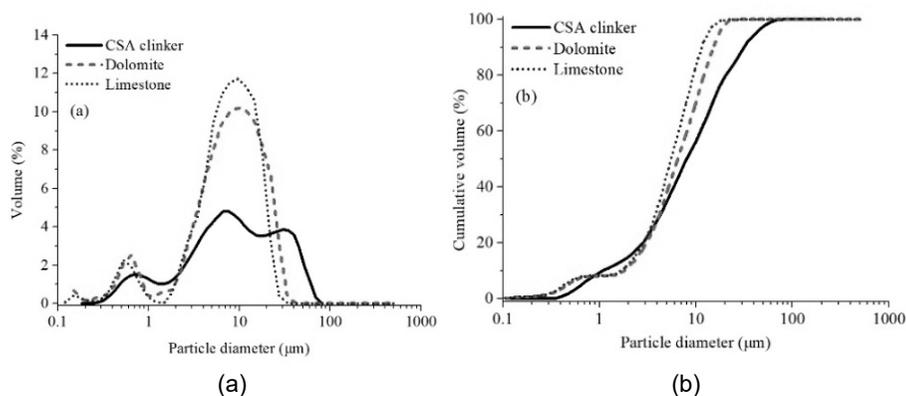


Figure 1: Particle size distribution of raw materials (a) differential particle size distribution (b).

Three CSA cement series were prepared at varying M values using a laboratory mixer, i.e. $M = 0$ (no gypsum), 1 and 2. The replacement of dolomite and limestone powders was fixed at 20% by mass of total CSA cement. For each matrix, both cement pastes and mortars were prepared with the constant w/cm ratio of 0.6. River sand (0-0.6 mm) was used with sand to cement ratio of 2:1. Cement pastes were cast in molds with a size of 20 mm × 20 mm × 20 mm to examine the evolution of hydrates. Mortars were

cast into 30 mm × 30 mm × 30 mm (compressive strength) into 20 mm × 20 mm × 80 mm (dimension stability) molds, respectively. After 12 h, the samples were demolded and then cured in tap water at 20 °C.

X-ray diffraction (XRD) patterns for the sample were obtained using an X-ray diffractometer (SmartLabTM 3 Kw Powder Diffractometer; Cu K α 1, $\lambda=1.5406$ Å). The X-ray tube was operated under 40 kV and 30 mA, the scanning speed of 5 °/min with a step of 0.02° was used.

A JEOL scanning electron microscope was used to observe the microstructure of hardened pastes. The elemental compositions of the selected morphologies were obtained with X-ray energy dispersive spectroscopy (EDS).

RESULTS

Figure 2 shows the strength measurements of mortars with different constituents. For the reference CSA, CSA1 mortar displays the highest long-term compressive strength among all investigated mortars, followed by CSA2 mortar, while CSA mortar without gypsum shows the lowest strength.

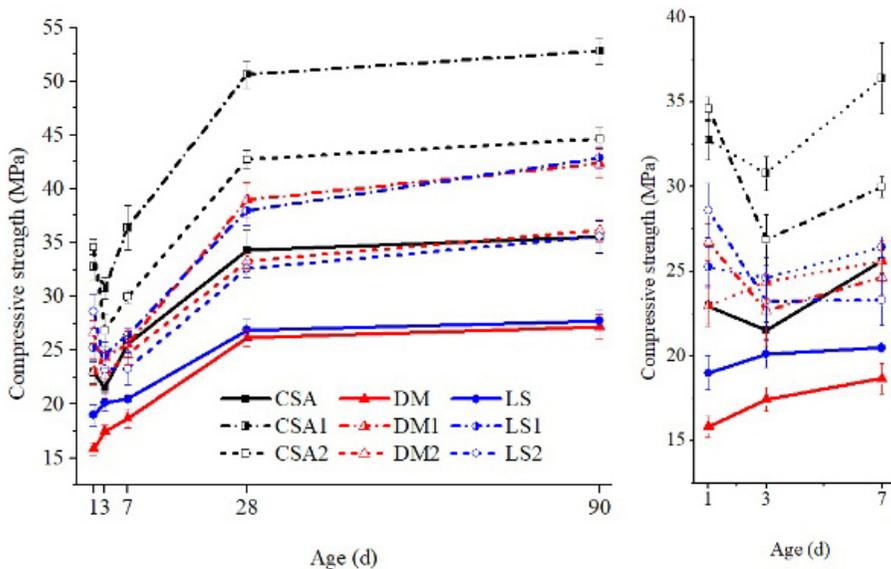


Figure 2: Compressive strength of the investigated mortars over hydration time.

This could be attributable to the optimum ratio of gypsum to CSA clinker. Whatever the gypsum content, the strength is decreased with the replacement by dolomite. Moreover, the dolomite-modified mortars develop a slightly lower early-age strength when compared to the mortars with limestone, but the difference decreases and disappears as the age increases. Additionally, the mortars without carbonate exhibit an obvious strength loss after 3 days. However, the mortars with dolomite or limestone

show no strength loss in the M0 system and less loss of strength in the M1 and M2 systems. For example, between 1 and 3 days, the strength loss in CSA, CSA1, and CSA2 is about 6.2%, 6.0% and 22.3%, respectively. CSA1-D exhibits no strength loss as well and the loss of strength in CSA1-L, CSA2-D, and CSA2-L is 2.4%, 15.0%, and 18.8%, respectively. After 3 days hydration, the strength increases continually for all the mortars tested. This indicates that similar to limestone, dolomite additions may reduce the loss of strength and improve strength evolution of CSA cement.

Figure 3 displays the dimension stability of mortars with different constituents. As shown in Figure 2, for the M1 and M2 systems with gypsum, all mortars show a rapid expansion up to about 7 days, and then the expansion reaches a plateau throughout the whole period. As expected, higher expansion is obtained for the mortars of the M2 system due to the presence of high gypsum content. The replacement of CSA cements by dolomite significantly reduces the expansion. However, it is interesting to note that CSA mortar without gypsum expands steadily and yields the highest expansion among all investigated mortars. Moreover, a lower decrease in expansion can be observed in DM mortars compared to LS mortars.

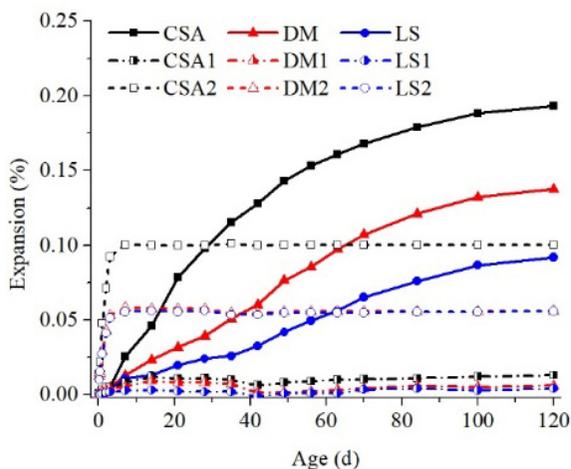


Figure 3: Dimension stability of the investigated mortars over hydration time.

Figure 4 shows the XRD patterns of the three systems with different M values cured for 7 days and 90 days. For the M0 system, all samples display the presence of ettringite and monosulfate (AFm12 or AFm14) phases, presumably due to the absence of gypsum. The CSA clinker sample shows the formation of strätlingite, which is associated with the reaction of belite and gibbsite according to [9]. The formation of hemicarbonate instead of strätlingite and the reduction of monosulfate can be observed in the sample containing dolomite or limestone. It is related to the reaction of carbonate, which provides CO_3^{2-} favoring the precipitation of carboaluminates rather than strätlingite and monosulfate [10, 11]. Moreover, the formed hemicarbonate is less

pronounced in the dolomite-modified sample, potentially ascribed to the slow dissolution rate of dolomite compared to limestone [12]. Besides, it should be noted that after 90 days the transformation of AFm14 into AFm12 occurs in all samples, which accompanied the increment of ettringite.

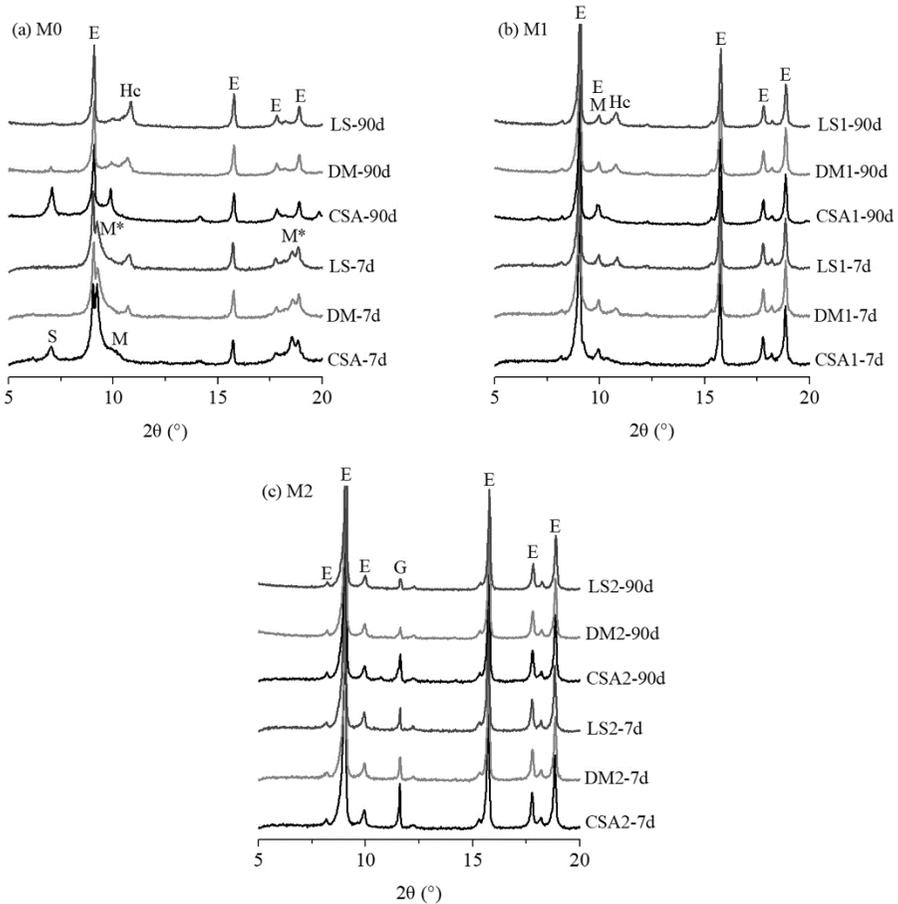


Figure 4: Cumulative heat of the specimens with different constitues (a) M0, (b) M1 and (c) M2. E: AFt; M: AFm₁₂; M*: AFm₁₄; Hc: hemicarbonate; S: strätlingite; G: gypsum.

For the M1 system with intermediate gypsum, strätlingite is not formed after 7 and 90 days, and all tested samples reveal similar main hydrated phases, including the large amount of ettringite and trace of monosulfate. Similarly, the formation of hemicarbonate has also been detected in the two carbonate-modified samples, but their peaks are weaker than those in the M0 system. Increasing gypsum content to the M2 system, after 7 days of hydration, clearly results in producing more ettringite than for samples hydrated in the M0 and M1 systems and no hemicarbonate can be found but

residual gypsum, and these hydrates do not change up to 90 days. According to the above results, it can conclude that dolomite can participate in hydration reaction to form hemicarbonate as does limestone when gypsum is insufficient, but it does not react or acts as a filler in the presence of enough gypsum. The result is consistent with previous work that has reported that increasing the gypsum content significantly reduces the extent of limestone reaction [8].

In order to study the expansion of CSA mortar without gypsum, SEM-BSE imaging was extended to examine the microstructure of CSA paste as shown in Figure 5. As shown in Figure 5a, a denser matrix can be observed after 90 days of hydration. The residual clinker is identified and it surrounds the cracks. The SEM-EDX elemental analysis shows that strätlingite are formed around the residual clinker, which is consistent with the XRD results. It has been reported that the formation of strätlingite could increase the total volume and contribute to expansion of CSA samples [13].

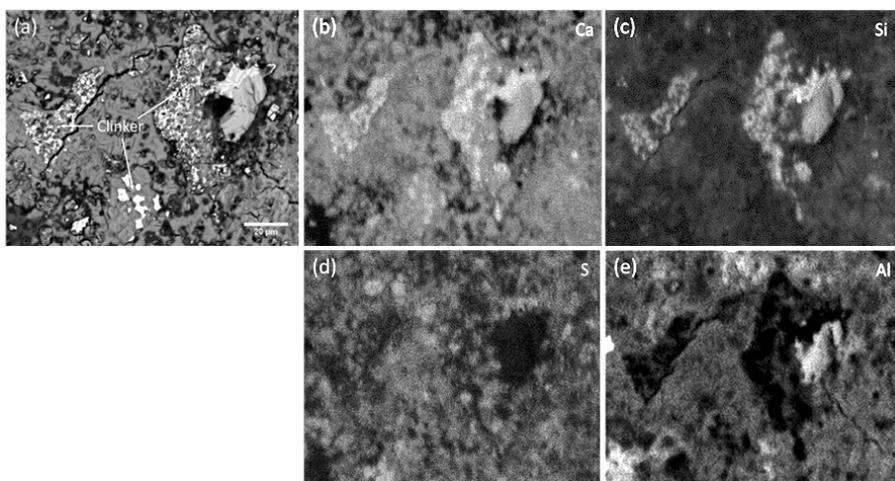


Figure 5: BSE image (a) and the corresponding elemental maps of Ca, Si, S and Al (b-e).

CONCLUSION

The reaction of dolomite is suppressed with increasing the amount of gypsum. In the system with insufficient gypsum, the formation of hemicarbonate takes place in dolomite samples similar to limestone samples, with less hemicarbonate forming in the dolomite samples due to its slow dissolution rate. The hemicarbonate formed stabilizes ettringite and minimizes the precipitation of strätlingite and monosulfate. In the presence of excess gypsum, however, dolomite does not react anymore and acts as a filler only.

In all investigated systems, the replacement of CSA cement by dolomite leads to decreasing compressive strength and expansion. However, the mortars containing dolomite and limestone have comparable compressive strength. Moreover, both

dolomite and limestone can reduce the strength loss of mortars at 3 days and improve strength development. In the absence of gypsum, a higher expansion can be observed with the replacement by dolomite compared with the limestone mortar. When the gypsum is added, the two mortars show similar expansion patterns.

ACKNOWLEDGEMENTS

This work is supported by the National Natural Science Foundation of China (51472116), the Graduate Student Scientific Research Innovation Projects in Jiangsu province and the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.

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