

Effect of gypsum on the strength of CSA treated sand

Taeseo Ku¹ and S. Subramanian¹

¹ Department of Civil and Environmental Engineering, National University of Singapore, 1 Engineering Drive 2, Singapore 117576.

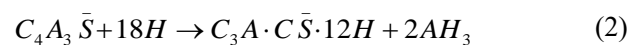
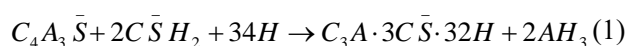
ABSTRACT

The conventional binding admixture for soil, Ordinary Portland Cement (OPC) has higher carbon footprint hence a new cement type namely Calcium sulfoaluminate (CSA) cement is examined as an effective alternate for OPC. Ye'elimite is the major constituent of CSA cement. The hydration of ye'elimite depends on the amount and reactivity of gypsum present. Depending on the amount of gypsum present, either monosulfate or ettringite is formed. Unconfined compressive strength (UCS) is used to measure the effectiveness of cementation. Since pure CSA is used in this study, the gypsum content is varied from 0% to 60% to find the optimum gypsum content. Optimum gypsum content is identified as the gypsum content which has higher initial strength and durable rate of strength gain with curing time. The results are then compared against OPC treated sand to examine CSA as an effective alternate for OPC. Scanning electron microscope (SEM) images and X-ray diffraction (XRD) technique are used to identify the type of hydration product formed.

Keywords: cemented sand, calcium sulfoaluminate, gypsum, ordinary portland cement, unconfined compressive strength

1 INTRODUCTION

Ground improvement through chemical stabilization is commonly used in Singapore to improve the soil characteristics. Ordinary Portland Cement (OPC) is the widely used binding admixture, which, in recent years, has been questioned for its sustainability, due to the CO₂ emission during manufacturing. In fact, OPC manufacturing accounts for 5% of manmade CO₂ emission (Damtoft et al. 2008). In concrete technology, calcium sulfoaluminate (CSA) is considered as an alternate to OPC, owing to its reduced carbon footprint. The main constituent of CSA is ye'elimite, which requires lower firing temperature, resulting in lesser consumption of fossil fuels (Juenger et al. 2011). The formation of ye'elimite results in 0.216 kg of CO₂ per kg of clinker produced, while Alite and Belite (main constituents in OPC) result in 0.578 kg and 0.511 kg of CO₂ per kg of clinker produced. The use of industrial by products such as blast furnace slag, silica fume and fly ash only replaces a partial fraction of OPC. Also, the type of hydration product formed depends on the amount of gypsum present in the mixture. Above a molar ratio of calcium sulfate to ye'elimite of two, ettringite is formed, below a molar ratio of two, monosulfate is formed. The hydration reactions are as follows (Winnefeld and Barlag 2010):



where C = CaO, A = Al₂O₃, \bar{S} = SO₃ and H = H₂O

Typically, 15-25% of gypsum or anhydrite is added to the CSA for dimensional stability and strength development. However, the properties of CSA treated soil are dependent on the amount and reactivity of gypsum or anhydrite added to the system (Glasser and Zhang 2001). The studies on CSA have focused on construction of bridges, water proof layers and concrete pipes, which requires very low water to cement ratios. Only a few researchers have examined the use of CSA for geotechnical application such as ground improvement or land reclamation, where high water to cement ratios are required. Subramanian et al. (2018) studied the use of one type of CSA for ground improvement purpose. However, there was a recoverable strength loss observed between 7 to 14 days of wet curing. Vinoth et al. (2018) studied the early strength development of two type of CSA cement treated sand using ultrasonic pulse velocity (UPV) and unconfined compressive strength. There was no gypsum optimization study carried by Subramanian et al. (2018) and Vinoth et al. (2018). This study will illustrate the effect of gypsum on the strength of CSA treated sand.

2 BACKGROUND

The literature available on CSA cement focused on

the hydration reaction and its microstructure. Lan and Glasser (1996) studied the hydration of CSA cement in presence of gypsum, lime, belite and calcium aluminates. Glasser and Zhang (2001) found that embedded steel inside concrete with CSA as binder was intact in a chloride rich environment. Winnefeld and Barlag (2010) investigated the influence of gypsum and anhydrite on the hydration of CSA cement till 18 hours. For long term behavior, Pelletier-Chaignat et al. (2011) studied the influence of gypsum and anhydrite on hydration behavior of CSA cement from an early stage till 28 days. Tang et al. (2015) studied the hydration stages and phase transformation between ettringite and monosulfate of calcium sulfoaluminate cement. Jeong et al. (2018) studied the strength development and hydration products of CSA cement pastes with different water and gypsum content.

3 MATERIALS AND SAMPLE PREPARATION

The sand used in this study has an effective particle size (D_{10}) of 0.45 mm and D_{50} of 0.71 mm. The coefficient of uniformity (C_U) and coefficient of curvature (C_C) of the sand are 1.78 and 1.00, respectively and is classified as poorly graded sand “SP” according to Unified Soil Classification System (USCS). The cement used are Ordinary Portland Cement Type I and Calcium Sulfoaluminate cement. Alite and Belite are the major constituent of OPC while ye’elimite is the major constituent of CSA cement.

In this study, water content is defined as the ratio of the mass of water to the mass of the total solids (dry soil + binder). The gypsum content is defined as the mass of gypsum present total mass of the binder (CSA + gypsum). This definition corresponds to gypsum being replaced for CSA cement. Fig. 1 explains the concept of adding and replacing gypsum. Cement content is defined as the mass of binder in the total mass of dry sand.

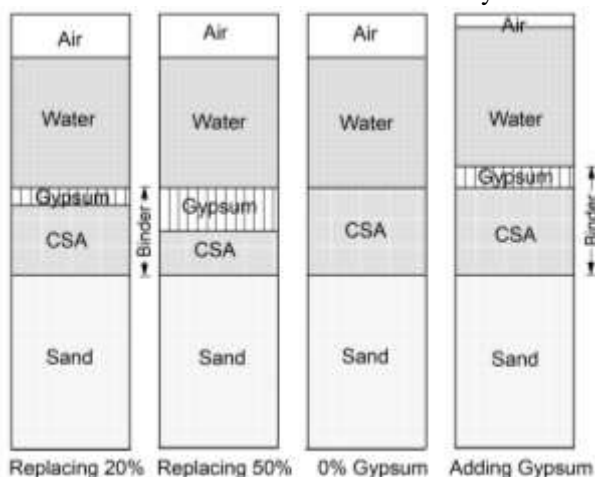


Fig. 1. Phase diagram explaining the concept of adding and replacing gypsum.

Preparing cemented sand involved three stages of mixing. The sample preparation technique has been discussed in detail by Subramanian et al. (2018).

Sacrificial samples were prepared for obtaining SEM images and XRD analysis. At the end of desired curing time, the sample was extracted and core of the sample was used for obtaining SEM images. For XRD, the samples were crushed in a ceramic mortar using pestle and soaked in isopropanol for two hours. Vacuum filtration is then carried out to remove the alcohol and then the sample is placed in a vacuum oven for one day. Immersing the sample in alcohol stops the hydration reaction. Then the sample is sieved through 150 microns sieve to remove the sand particles and the cementitious powder collected is used for XRD analysis.

4 RESULTS AND DISCUSSION

The presence of gypsum or anhydrite controls the type of hydration product, which in turn affects the strength of CSA treated soil. Since pure CSA is used in this study, the effect of gypsum content is investigated by varying it from 0% to 60% to find the optimum gypsum content. The cement content and water content are fixed at 7% and 10%, respectively. Optimum gypsum content is identified as the gypsum content that yields reasonably high initial strength and durable rate of strength gain with curing time. Fig. 2 shows the variation of strength with curing time for various gypsum contents.

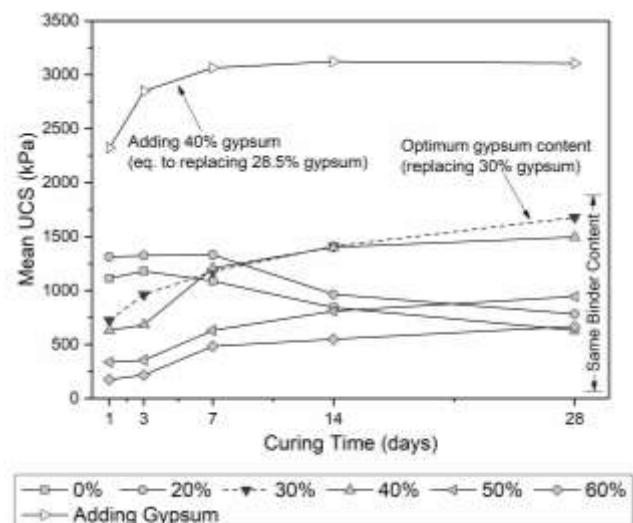


Fig. 2. Variation of strength with curing time for various gypsum contents.

CSA treated sand up to 20% gypsum shows higher initial strength up to 7 days of curing followed by strength loss till 28 days. Between 50% to 60% gypsum content, the samples show low initial strength followed by strength gain with time. The optimized gypsum content is identified as 30% as the initial strength is high followed by strength gain till 28 days. The changes in the compressive strength can be explained by conducting some microstructure analysis. Fig. 3 and Fig. 4 show the

SEM images and XRD results of CSA treated sand cured for 1 day with various gypsum content to identify the type of hydration products formed.

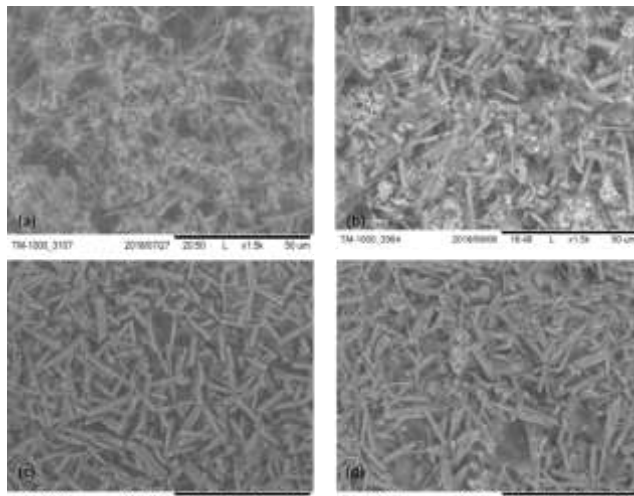


Fig. 3. SEM images after one day curing for CSA treated sand samples with (a) 0%, (b) 20%, (c) 30%, and (d) 40% gypsum content.

Though equation 2 indicates that in absence of gypsum only monosulfate can be formed, needle shaped ettringite can be seen in traces from the SEM image of 0% gypsum content. The XRD result further confirms the presence of ettringite.

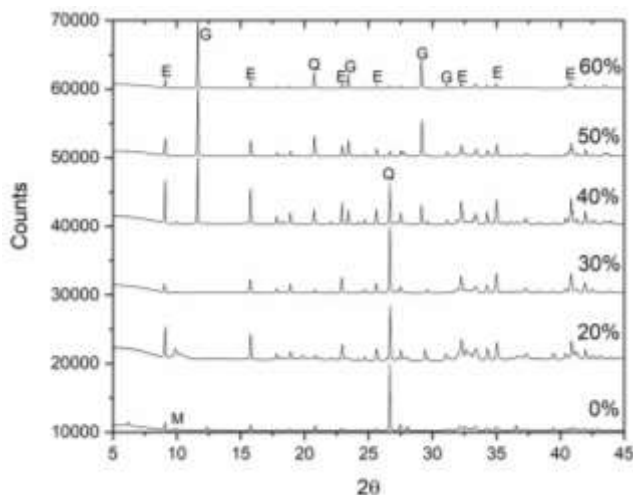
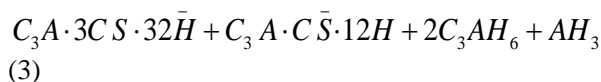
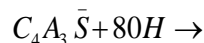


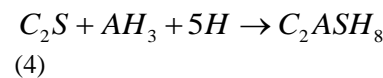
Fig. 4. X-ray diffraction of CSA cemented sand cured for one day with various gypsum content. (E=Ettringite, G=Gypsum, Q=Quartz, and M=Monosulfate).

Wadsö (2005) postulated that ettringite can be formed from the hydration of pure ye'elimite through equation 3:



From the SEM image it can be observed that the sample with 30% gypsum content produces only ettringite as no apparent monosulfate peaks are visible in the XRD. Beyond 30% gypsum content, only ettringite is formed as shown in Fig. 3, but there are traces of unreacted gypsum present as shown in Fig. 4. In summary, up to 30% gypsum content, the gypsum added is completely utilized within the hydration process. In samples with lower gypsum content, strength loss is observed after 7 days of curing. Fig. 5 shows the XRD results of hydrated pure CSA cemented sand at 1, 7 and 28 days curing compared against 28 days cured samples of higher gypsum content.

The XRD results show the formation of stratlingite at 7 days of curing in lower gypsum content. Stratlingite peaks dominate at the end of 28 days and could be major contributor for strength in low gypsum content samples in long term. Stratlingite is formed from the hydration of belite in presence of aluminum hydroxide (Jeong et al. 2018) as shown in equation 4:



Previous studies have also reported stratlingite formation after 7 days of curing (Winnefeld and Barlag 2010). Jeong et al. (2018) reported the formation of significant amount of stratlingite in samples with low to medium gypsum content (15% to 20%) at high water to cement ratio.

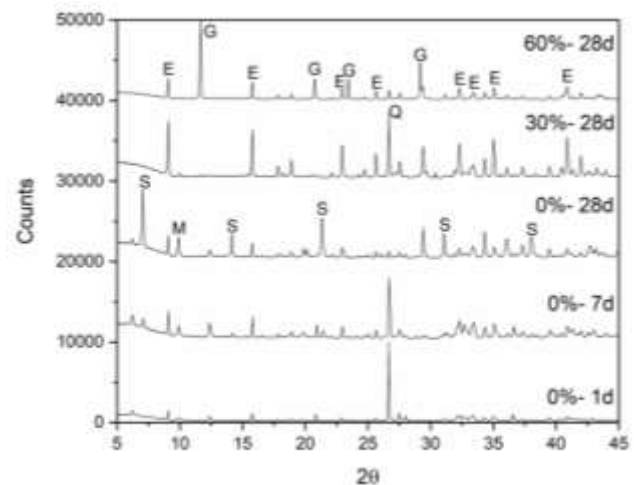


Fig. 5. X-ray diffraction at various curing stages for 0% gypsum content compared with 28 days curing of 30% and 60% gypsum content. (E=Ettringite, G=Gypsum, Q=Quartz, S=Stratlingite, and M=Monosulfate).

Despite the above findings, the reason for the strength loss is not clear yet, but it could be because of the microstructural changes. Comparing Fig. 4 and Fig. 5, it is clear that ettringite is the major hydration product

and contributes to the initial strength and the strength development in later stages. Till the end of 28 days unreacted gypsum is present in samples with high gypsum content. The presence of unreacted gypsum did not have any detrimental effect on the strength of CSA treated sand.

As gypsum replaces CSA in the binder, samples with lower gypsum content show higher initial strength as the amount of ye'elimite available for hydration is higher. As the gypsum content increases, the ye'elimite percentage reduces leading to lower initial strength gain. For example, as shown in Fig. 2, instead of replacing CSA with gypsum, suppose that gypsum is added to CSA cement. In this way, the ye'elimite concentration is kept constant. When 40% gypsum is added to CSA (equivalent to 28.5% replacing gypsum), the initial strength is higher than that of 0% gypsum content with strength gain till 28 days. Thus, with same ye'elimite concentration, the addition of optimum gypsum content results in increased strength compared to sand treated with pure CSA cement. As discussed earlier, the cement content is defined in terms of total mass of binder, which in turn refers to replacing CSA with gypsum.

Therefore, 30% of gypsum is determined as the optimized gypsum content as the initial strength gain is high followed by durable rate of strength gain up to 28 days. Based on the microstructure study, the gypsum present in the mix is completely utilized for hydration of ye'elimite.

5 CONCLUSIONS

The hydration chemistry of CSA cement, whose major constituent is ye'elimite, is complicated as it depends on the amount of gypsum present in the clinker. This paper examined the strength of CSA treated sand with gypsum contents ranging from 0% to 60%.

- Up to 20% gypsum content, CSA treated sand has strength loss with time, while 30% to 40% gypsum content samples have high initial strength with subsequent strength gain. Higher gypsum content samples have low initial strength followed by strength gain.
- XRD analysis of samples indicates that monosulfate and ettringite are formed in samples with gypsum content 20%. Ettringite is the only hydration product formed from 30% gypsum content, while unreacted gypsum is present in samples having gypsum content above 40%.
- At 28 days of curing, stratlingite is formed for samples with low gypsum content and unreacted gypsum is still present in samples with high gypsum content.
- Ettringite to monosulfate conversion was not observed in samples with 30% gypsum content.

6 REFERENCE

- Damtoft, J. S., Lukasik, J., Herfort, D., Sorrentino, D., and Gartner, E. M. (2008). "Sustainable development and climate change initiatives." *Cement and Concrete Research*, Elsevier Ltd, 38(2), 115–127.
- Glasser, F. P., and Zhang, L. (2001). "High-performance cement matrices based on calcium sulfoaluminate–belite compositions." *Cement and Concrete Research*, Elsevier, 31(12), 1881–1886.
- Jeong, Y., Hargis, C. W., Chun, S.-C., and Moon, J. (2018). "The effect of water and gypsum content on stratlingite formation in calcium sulfoaluminate–belite cement pastes." *Construction and Building Materials*, Elsevier, 166, 712–722.
- Juenger, M. C. G., Winnefeld, F., Provis, J. L., and Ideker, J. H. (2011). "Advances in alternative cementitious binders." *Cement and Concrete Research*, 41(12), 1232–1243.
- Lan, W., and Glasser, F. P. (1996). "Hydration of calcium sulfoaluminate cements." *Advances in cement Research*, Thomas Telford Ltd, 8(31), 127–134.
- Pelletier-Chaignat, L., Winnefeld, F., Lothenbach, B., Le Saout, G., Müller, C. J., and Famy, C. (2011). "Influence of the calcium sulphate source on the hydration mechanism of Portland cement–calcium sulfoaluminate clinker–calcium sulphate binders." *Cement and Concrete Composites*, 33(5), 551–561.
- Subramanian, S., Moon, S. W., Moon, J., and Ku, T. (2018). "CSA treated sand for ground improvement: Microstructure analysis and rapid strength development." *Journal of Materials in Civil Engineering*, American Society of Civil Engineers.
- Tang, S. W., Zhu, H. G., Li, Z. J., Chen, E., and Shao, H. Y. (2015). "Hydration stage identification and phase transformation of calcium sulfoaluminate cement at early age." *Construction and Building Materials*, Elsevier, 75, 11–18.
- Vinoth, G., Moon, S.-W., Moon, J., and Ku, T. (2018). "Early strength development in cement-treated sand using low-carbon rapid-hardening cements." *Soils and Foundations*, Elsevier.
- Wadsö, L. (2005). "Applications of an eight-channel isothermal conduction calorimeter for cement hydration studies." *Cement international*, Verlag Bau und Technik GmbH, (5), 94–101.
- Winnefeld, F., and Barlag, S. (2010). "Calorimetric and thermogravimetric study on the influence of calcium sulfate on the hydration of ye'elimite." *Journal of thermal analysis and calorimetry*, Springer, 101(3), 949–957.