Characterization of calcium sulfoaluminate cements exposed to accelerated weathering carbonation conditions

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Contents

Introduction

Research background

- Need for new cementitious binder systems[1,2]
  - Reduction of net CO_2 emissions is inevitable in cement industry
  - Demand for cement continues to grow, and Portland cement (PC) is the most commonly used construction material in the world
  - Cement industry is responsible for about 5 – 8% of worldwide man-made CO_2 emissions
- Classification of alternative cementitious binder systems[2,3]
  - PC blended with supplementary cementitious materials
  - Alkali-activated cements such as alkali-activated slag, geopolymer and etc.
  - Calcium aluminate cement (CAC)
  - Calcium sulfoaluminate (CSA) cement and belite-ye'elimite-ferrite (BYF) cement
  - Magnesium (or calcium) phosphate cement (MPC) including magnesium (potassium) phosphate binders

1. Gartner and Sui, Alternative cement clinkers, Cem. Concr. Res. (2017) In Press.
2. Juenger et al., Advances in alternative cementitious binders, Cem. Concr. Res. 41 (2011) 1232-1243.
3. Provis, Alkali-activated materials, Cem. Concr. Res. (2017) In Press.

Properties of CSA cements

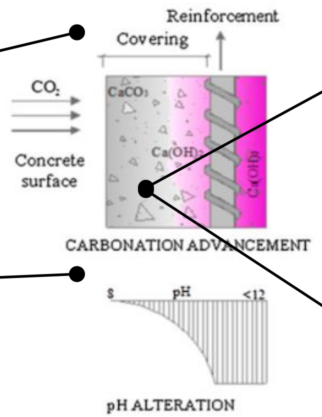
- Typical properties of CSA cements[4]
  - Fast bond
  - Rapid strength development
  - Shrinkage compensation (expansive cement)
  - Short curing phase
  - Low alkali contents
  - Low CO_2 emissions

4. chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/viewer.html?pdfurl=https%3A%2F%2Fcaltra.com%2Fwp%2Fwp-content%2Fuploads%2F2016%2F11%2FWhat-is-CSA-Cement..pdf&clen=505572&chunk=true

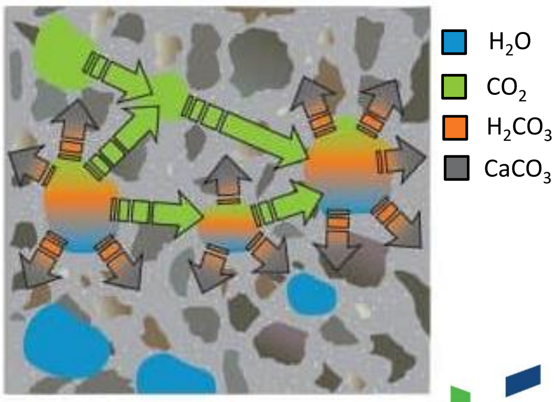
Weathering carbonation

- Weathering carbonation of cementitious materials (passive, ageing)
  - Weathering carbonation is an inevitable deterioration phenomenon to cementitious materials, slowly affecting the durability of the cementitious materials[5].
  - The dissolved CO_2 in the pore solution of the cementitious materials reacts either with portlandite or with C-S-H, leading to the reduction of pH level and to the corrosion of embedded rebars[6].

[Fig] Carbonation-induced corrosion of concrete surface and rebars[7].



[Fig] Carbonation-induced corrosion of concrete surface and rebars[8].



[Fig] Carbonation front in PC concrete[7]

5. Rostami, V., Shao, Y., Boyd, A. J., & He, Z. (2012). "Microstructure of cement paste subject to early carbonation curing." Cement and Concrete Research, 42(1), 186-193.
6. Richardson, M. G. (1988). "Carbonation of reinforced concrete: its causes and management". Citis.
7. https://civildigital.com/carbonation-concrete-various-failure-mechanisms-concrete/
8. Possan, E., Thomaz, W.A., Aleandri, G.A., Felix, E.F. and dos Santos, A.C., 2017. CO2 uptake potential due to concrete carbonation: A case study. Case Studies in Construction Materials, 6, pp.147-161.

Factors affecting carbonation behavior of CSA cements

Zhang et al.[9] : Water-to-cement ratio

- Zhang et al. (2009)[9] investigated the carbonation behavior of CSA cement with different w/c ratio ranging 0.33 – 0.49.
- Lower water content decreased the carbonation depth, which signifies the higher carbonation resistance.
- Ettringite, formed under the sufficient w/c ratio conditions, was confirmed to be vulnerable against carbonation.

9. Zhang, D., Xu, D., Cheng, X., & Chen, W. (2009). Carbonation resistance of sulphoaluminate cement-based high performance concrete. Journal of Wuhan University of Technology-Mater. Sci. Ed., 24(4), 663-666.

Hargis et al.[10] : *m*-values

- Hargis et al. (2017)[10] investigated the carbonation resistance of the CSA cements with different *m*-values (1.0, 1.4, or 1.8).

- An increase in the *m*-value accelerated the reaction of ye'elimite and densified the microstructure, resulting in an increase in the carbonation resistance.

- Hydration products such as monocarbonate and ettringite were found to be first phases being converted into calcium carbonate upon the carbonation.

10. Hargis, C. W., Lothenbach, B., Müller, C. J., & Winnefeld, F. (2017). Carbonation of calcium sulfoaluminate mortars. Cement and Concrete Composites, 80, 123-134.

Park[11] : Replacement with SCM

- Park (2020)[11] theoretically investigated the carbonation resistance of CSA cements blended with supplementary cementitious material (SCM).

- Replacement with SCM lowered the carbonation resistance, leading to the decrease in pH and to the volumetric instability of the matrix.

- Monosulfate acted as an initial carbonation buffer and was transformed into monocarbonate, which became calcium carbonate upon exposure to the high CO_2 concentration.

11. Park, S. (2020). Simulating the carbonation of calcium sulfoaluminate cement blended with supplementary cementitious materials. Journal of CO2 Utilization, 41, 101286.

CSA cements exposed to an accelerated carbonation condition: Role of MgO[12]

12. Seo, J., Yoon, H. N., Kim, S., Wang, Z., Kil, T., Lee, H. K. (2021). Characterization of reactive MgO-modified calcium sulfoaluminate cements upon carbonation. Cement and Concrete Research, 146, 106484.

Research objective and methodology[12]

▪ Objective

▶ To provide the detailed information of the carbonation of CSA cements and role played by MgO upon carbonation

▪ Methodology

[Table] Chemical composition of CSA clinker used in this study (wt.%)

	CaO	Al_2O_3	SO_3	SiO_2	MgO	Fe_2O_3	TiO_2	SrO	K_2O	P_2O_5	Na_2O	ZrO_2	LOI*
CSA clinker	**43.0**	**30.2**	**9.0**	**8.4**	**2.1**	**1.9**	**1.4**	**1.0**	**0.4**	**0.2**	**0.1**	**0.1**	**2.2**

* Loss-on-ignition

CSA clinker & Gypsum + MgO → Cured for 56 days → MgO-modified CSA paste sample → Exposure to 3% for 28 days → Carbonation

- MgO dosage : 0, 5, 10, or 20% → Sample ID : M0, M5, M10, or M20
- Water-to-binder ratio : 0.5
- *m*-value: 1.0

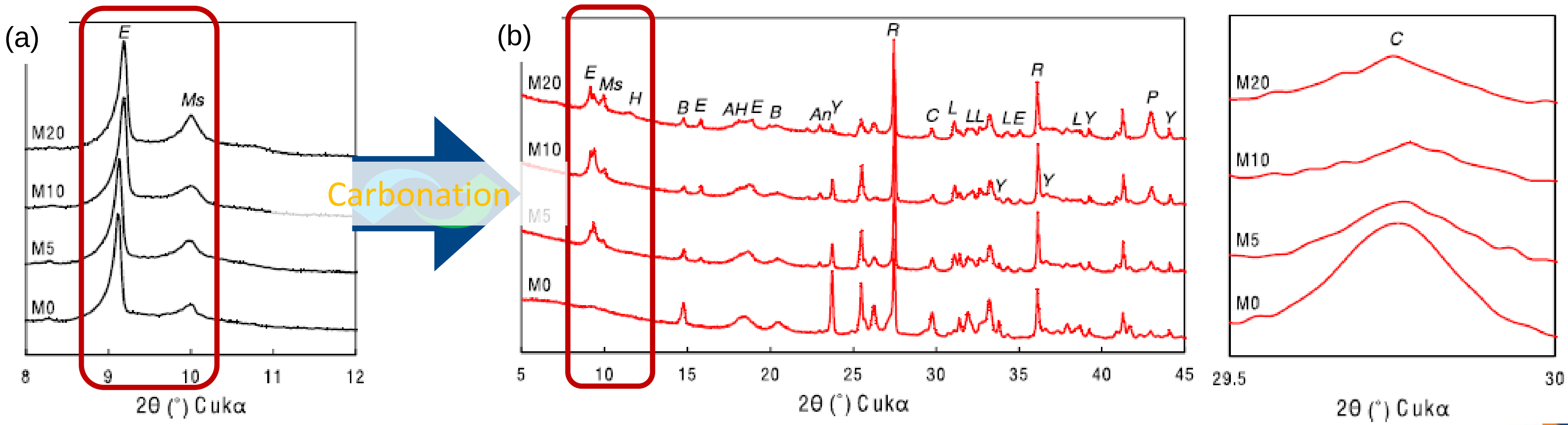
• Characterization tools

- ❑ X-ray diffractometry (XRD)
- ❑ Thermogravimetry (TG)
- ❑ Nuclear magnetic resonance (NMR) spectroscopy
- ❑ Scanning electron microscopy (SEM)/ energy-dispersive X-ray spectroscopy (EDS)
- ❑ Carbonation depth

12. Seo, J., Yoon, H. N., Kim, S., Wang, Z., Kil, T., Lee, H. K. (2021). Characterization of reactive MgO-modified calcium sulfoaluminate cements upon carbonation. Cement and Concrete Research, 146, 106484.

X-ray diffractometry[12]

- MgO incorporation preferred the formation of monosulfate over ettringite.
- Ettringite and monosulfate still existed after carbonation in the samples with MgO.
- A reduction in calcite peak intensity signified a decrease in the degree of carbonation.

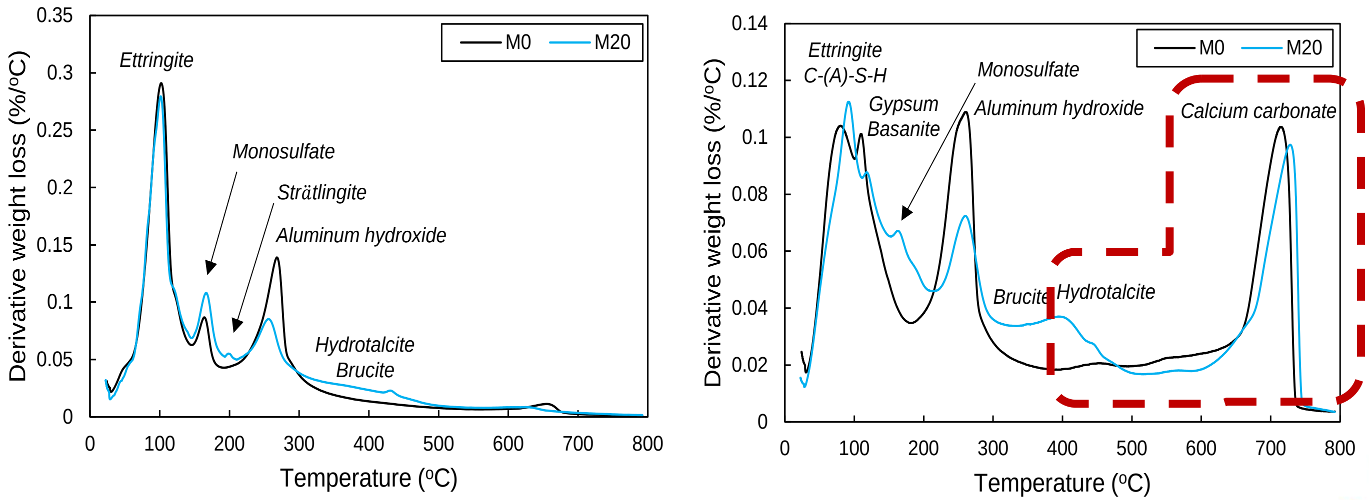


[Fig] X-ray diffractometry patterns of the (a) uncarbonated and (b) carbonated MgO-modified CSA cement paste samples

12. Seo, J., Yoon, H. N., Kim, S., Wang, Z., Kil, T., Lee, H. K. (2021). Characterization of reactive MgO-modified calcium sulfoaluminate cements upon carbonation. Cement and Concrete Research, 146, 106484.

Thermogravimetry[12]

- MgO incorporation preferred the formation of monosulfate over ettringite and aluminum hydroxide.
- The formation of hydrotalcite became clear in the samples with MgO.
- The amount of calcium carbonates reduced by MgO incorporation (M0 : 13.21%, M20 : 9.54%).



[Fig] Thermogravimetry and derivative thermogravimetric analysis of the (a) uncarbonated and (b) carbonated MgO-modified CSA cement paste

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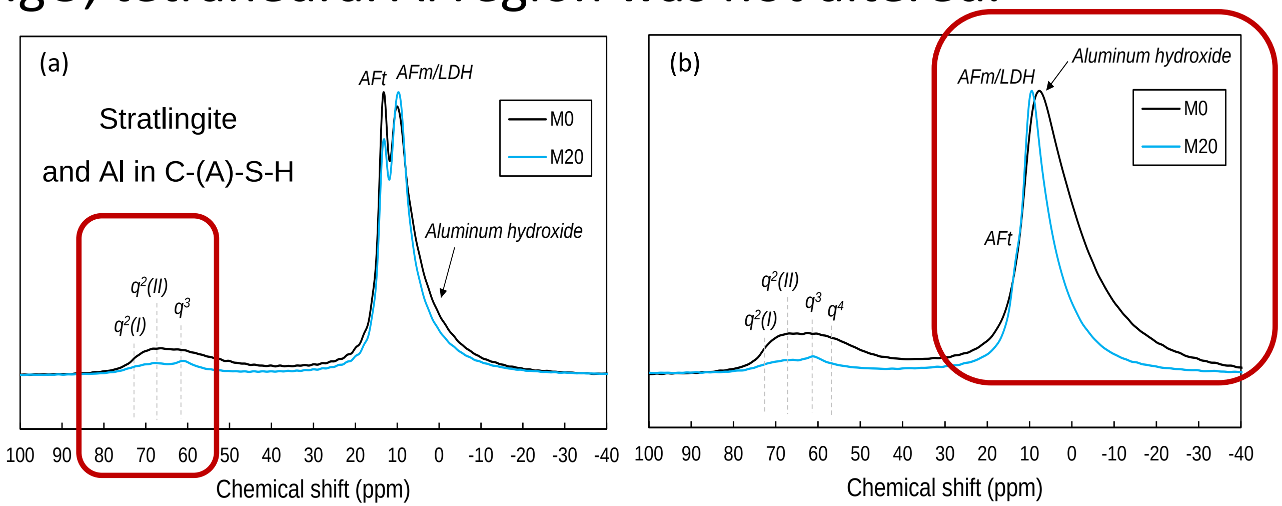
^{27}Al MAS NMR[12]

- MgO reduced the degree of Al incorporation in C-S-H.
- Upon carbonation, AFm/LDH strongly persisted in the sample with MgO.
- Degree of Al incorporation in C-(A)-S-H of the sample without MgO i ncreased upon carbonation.
- With MgO, tetrahedral Al region was not altered.



[Fig] Normalized solid-state ^{27}Al MAS NMR spectra
of the (a) uncarbonated and (b) carbonated MgO-modified CSA cement paste samples

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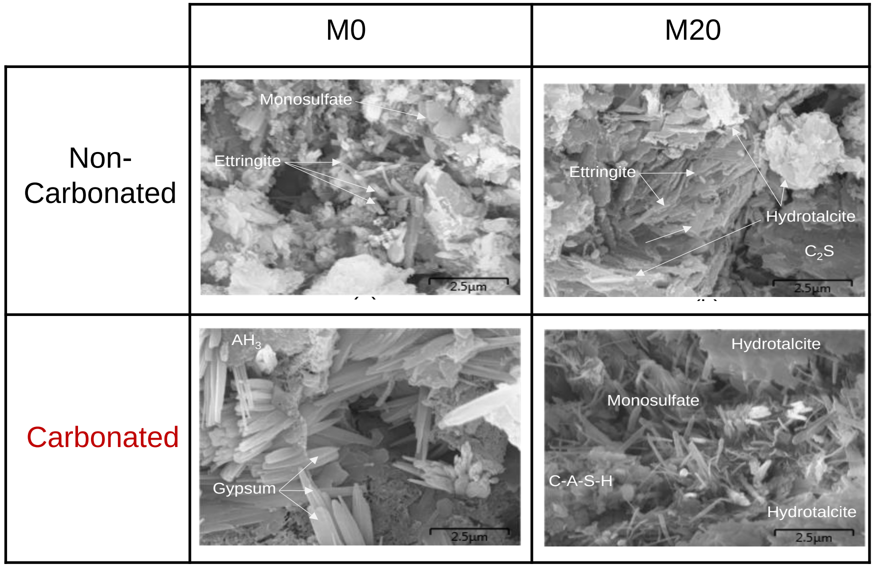
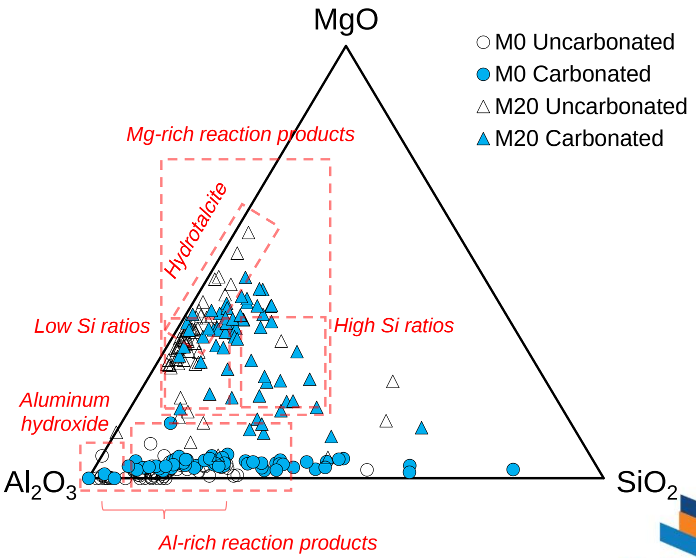
SEM/EDS[12]

- The samples without MgO mainly showed gypsum and aluminum hydroxide after carbonation.
- The samples with MgO mainly consist of AFm phases with C-(A)-S-H after carbonation.
- MgO triggered the formation of hydrotalcite and Mg-rich reaction products with high Si ratios.



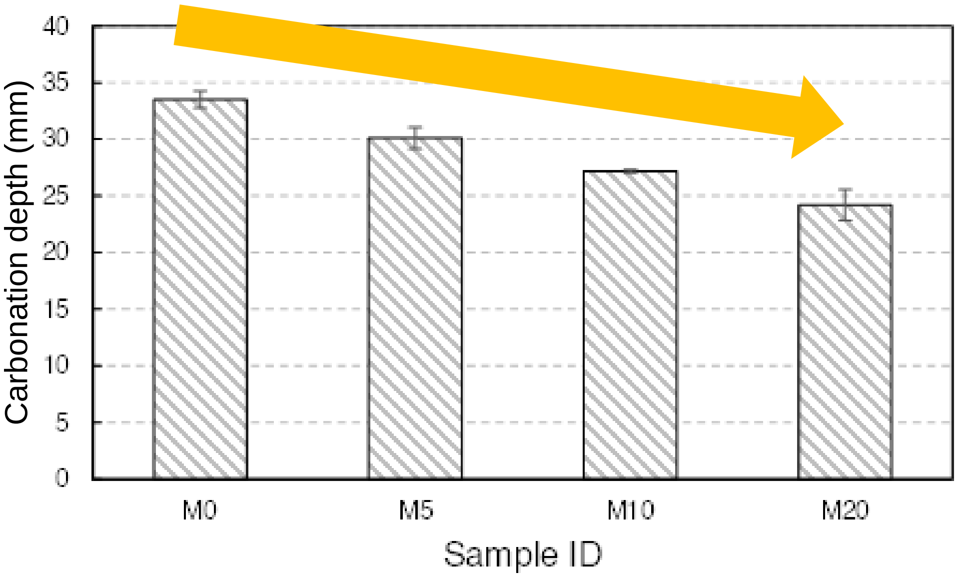


[Fig] (Left) SEM images of the samples and (Right) Ternary plot of the Mg:Al:Si stoichiometry of the reaction products in MgO-modified CSA cement pastes as analyzed by an elemental composition EDS analysis

12. Seo, J., Yoon, H. N., Kim, S., Wang, Z., Kil, T., Lee, H. K. (2021). Characterization of reactive MgO-modified calcium sulfoaluminate cements upon carbonation. Cement and Concrete Research, 146, 106484.

Carbonation depth[12]

- Carbonation depth decreased as the MgO content increased
- Hydrotalcite, which was formed by MgO incorporation, captured CO_2, leading to an enhancement in the carbonation resistance.



[Fig] Carbonation degree of the carbonated MgO-modified CSA cement paste samples

12. Seo, J., Yoon, H. N., Kim, S., Wang, Z., Kil, T., Lee, H. K. (2021). Characterization of reactive MgO-modified calcium sulfoaluminate cements upon carbonation. Cement and Concrete Research, 146, 106484.

Concluding remarks

Concluding remarks

- Weathering carbonation is an inevitable deterioration phenomenon of cementitious materials which should be taken into account when adopting a new binder system.
- A lower w/c ratio and higher *m*-value of CSA cement can enhance carbonation resistance, while the replacement with supplementary cementitious material can degrade the carbonation resistance of CSA cement.
- Carbonation of CSA cement induced the full carbonation of ettringite and monosulfate.
- Incorporation of MgO in CSA cement led to the formation of AFm phase including hydrotalcite over ettringite and aluminum hydroxide, thereby mitigating the ingress of CO_3^{2-} ions
- The presence of hydrotalcite in the MgO-modified CSA cement can improve the carbonation resistance.

Reference

1. Gartner and Sui, Alternative cement clinkers, *Cement and Concrete Research,* (2017) In Press.
2. Juenger et al., Advances in alternative cementitious binders, *Cement and Concrete Research,* 41 (2011) 1232-1243.
3. Provis, Alkali-activated materials, *Cement and Concrete Research,* (2017) In Press.
4. chrome-extension://efaidnbmnnnibpcajpcglclefindmkaj/viewer.html?pdfurl=https%3A%2F%2Fcaltra.com%2Fwp%2Fwp-content%2Fuploads%2F2016%2F11%2FWhat-is-CSA-Cement..pdf&clen=505572&chunk=true
5. Rostami, V., Shao, Y., Boyd, A. J., He, Z. Microstructure of cement paste subject to early carbonation curing. *Cement and Concrete Research*, 42(1) (2012) 186-193.
6. Richardson, M. G. Carbonation of reinforced concrete: its causes and management. Citis. (1988).
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Thank You!