Susceptibility of Heat-Cured Concrete to Deleterious DEF; the Role of Alkali, Sulfate, and Temperature

Liam Martin[1], Paul Thomas[2], Pre de Silva[3], Vute Sirivivatnanon[2]

[1] University of Technology Sydney, Sydney, Australia, *liam.martin@uts.edu.au*
[2] University of Technology Sydney, Sydney, Australia
[3] Australian Catholic University, Sydney, Australia

Abstract. Durability of concrete materials is important for their global use in infrastructure. One potential cause of durability loss is delayed ettringite formation (DEF), a form of internal sulfate attack. DEF can lead to deleterious expansion, microcracking, and strength loss in affected elements and is of most concern in precast concrete, with major factors including pore solution alkalinity, elevated curing temperatures, and sulfate and aluminate binder contents. The role of chemical factors and heat in deleterious DEF has been investigated in this study with concrete prisms and hydrated cement paste samples via linear expansion and phase development. Results show that a combination of sustained heat and elevated alkali and sulfate contents are necessary for deleterious DEF to occur.

Keywords: Delayed Ettringite Formation, Precast Concrete, Cement Chemistry, Durability.

1   Introduction

Delayed ettringite formation (DEF) is a form of internal sulfate attack that potentially can cause severe loss of durability in affected concrete structures, via expansion, microcracking, and strength loss . Early ettringite formation (EEF) is an early hydration reaction in cement between aluminate and sulfate ions, producing the sulfate mineral ettringite, as in Eq. (1) [1].

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_3A \cdot 3C\bar{S} \cdot 32H \tag{1}$$
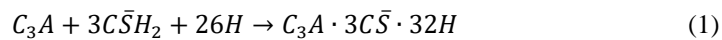
The key mechanism of DEF is the stability of ettringite during the early stages of curing, which is linked to the solubility of sulfate in the pore solution. Increasing alkalinity or temperature leads to the dissolution of sulfate ions, resulting in the decomposition of ettringite (an alumino-trisulfate (AFt) phase) in favour of alumino-monosulfate phases (AFm), and (re)precipitation with reduced alkalinity and or temperature, see Eq. (2). If ettringite is removed during early hydration, it can later reform in hardened paste as an expansive phase with deleterious results [2].

$$ettringite \rightleftharpoons AFm + sulfate\ ions \tag{2}$$
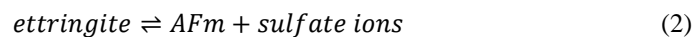
Sulfate and aluminate content are reactant factors in DEF, influencing the extent of ettringite formation. Alkali and temperature are processing factors in DEF, influencing the stability of ettringite. Laboratory mortar experiments into deleterious DEF have reported a pessimum binder content of 1% Na_2O_{eq}, 4% SO_3, $[SO_3]/[Al_2O_3] \geq 1$, and a temperature threshold of 70 °C [3]., informing industry guidelines for Australian and international producers of heat-cured concrete elements [4]. DEF is of principle concern for precast concrete, where it has been reported that the internal temperature of large elements can reach $\geq$ 85 °C for $\geq$ 8 hrs [5].

This paper investigates the role of sulfate & alkali contents and temperature on the observed expansion in concrete specimens of both low-risk and at-risk of deleterious DEF mixes, and the hydration reactions in comparable paste systems.

2   Experimental

Cement used was an Australian commercial GP cement (0.47 % Na_2O_{eq}, 2.6 % SO_3). Chemical content of the binder was altered by addition of 1 M NaOH solution (1% Na_2O_{eq}) and gypsum powder (4% SO_3) during mixing. Concrete specimens (450 kg/m^3 cement, 0.40 w/c, 120 mm slump) were prepared using the approach outlined in AS 1012.2-2014, with prisms (3 sets, 75×75×285 mm) measured for linear length and mass (day 7 reference). Compressive strength was determined according to AS 1012.9-2014, for cylinders (2 sets, 100×200 mm) at day 1 & day 28, and cut prism cubes (2 sets, 75 mm) at 1 year. Cement paste specimens (10 g, 0.40 w/c) were also prepared. Samples were cured in a humid atmosphere either at ambient (23 °C) or with a heat-curing cycle: preset at 30 °C for 4 hrs, ramp to 90 °C at 30 °C/hr, soak at 90 °C for 12 hrs, cooled to ambient and demoulded. All samples were stored in separate limewater tanks (23 ± 2 °C) after demoulding. Paste sample hydration was arrested via isopropanol solvent exchange, and characterized by XRD (Cu K-α2 source, Ni filter, 0.02 step) and TG (He flow 40 mL/min, 20 K/min).

3   Results & Discussion

Sets of concrete specimens subject to various binder and curing conditions to promote DEF were monitored for linear expansion, mass gain, and compressive strength over 1 year (at day 1, day 28, 1 year), with the results shown in Fig. 1. Comparable paste specimens were also made, with hydrated phases characterized at day 1 and day 28 via XRD and TG, as shown in Fig. 2.

Concrete subject to both heat-curing and pessimum chemical conditions showed significant expansion (2.0%), mass gain (2.5%), and loss of compressive strength (-46.5%). All other concrete systems did not show deleterious effects. Observed expansion was early and high at 90 days, and at 1 year was slowed but ongoing. Mass gain strongly correlated with expansion, which was attributed to water ingress via microcracking.

In hydrated cement, ettringite was prominent in ambient cured and absent in early heat-cured systems, but started to develop later which was associated with the slow

precipitation of dissolved sulfate. AFm phases (Mc, Hc) were identified in all systems, but were most prominent in heat-cured pessimum.
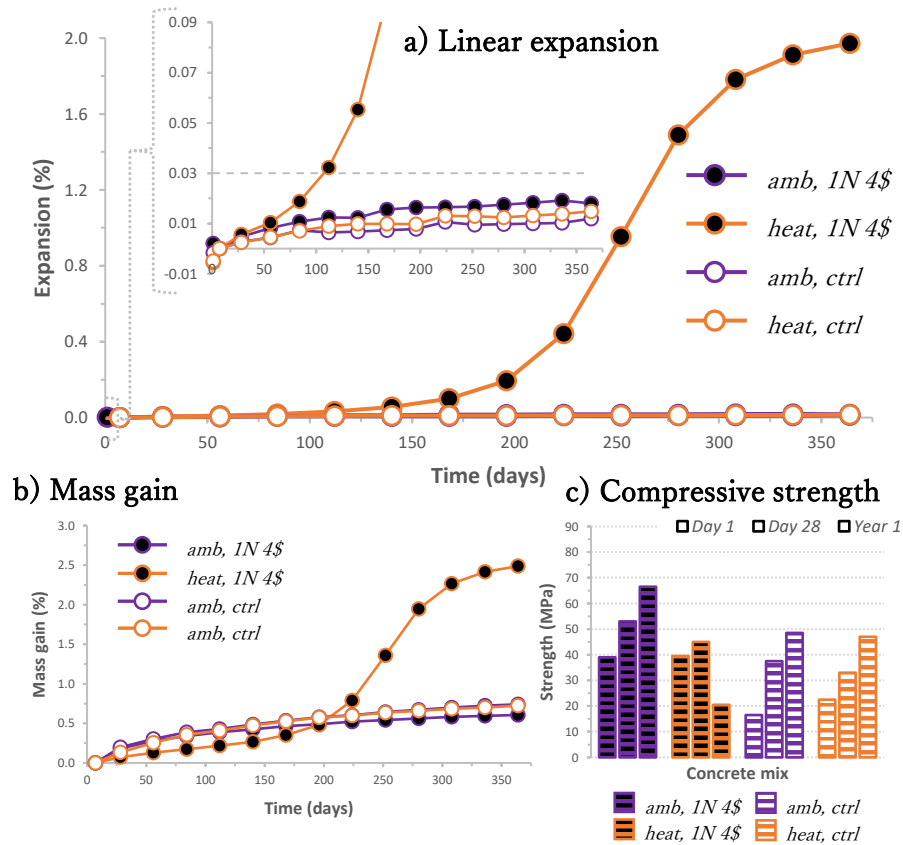

Fig. 1. Linear expansion (a, insert of magnified view), mass gain (b), and compressive strength (c) of concrete prisms subject to different binder and curing conditions. Curing was either at ambient (amb), or heat-cured (heat) at 90 °C for 12 hrs. Binder was either unaltered GP cement as control (ctrl), or 1% alkali and 4% sulfate content (1N 4$). Only concrete systems with heat-curing and pessimum conditions showed deleterious effects after 1 year, all other systems did not.

4   Conclusion

In summary, concrete specimens subject to sustained, elevated heat-curing and pessimum binder conditions showed significant expansion and strength loss after 1 year, which was attributed to deleterious DEF. Phase analysis of cement paste samples identified the presence of ettringite in ambient-cured samples and absence in heat-cured samples, but with minor development at later ages.
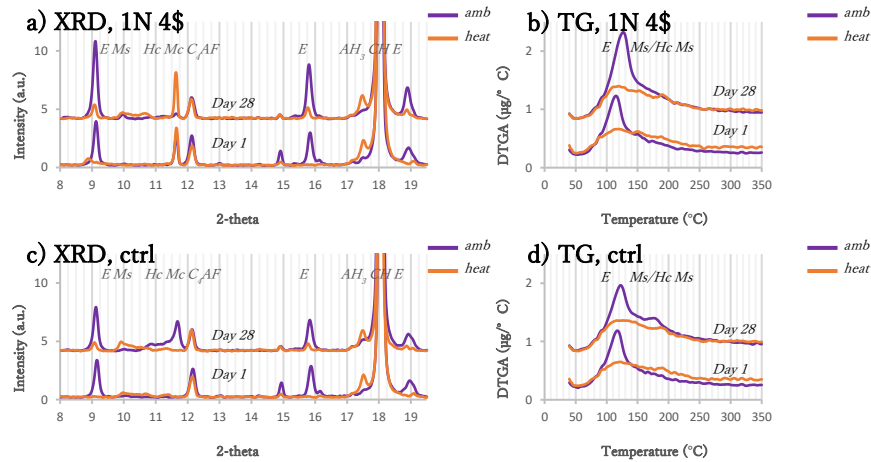
Fig. 2. Phase analysis of cement paste samples subject to different binder and curing conditions, with XRD (a, c) and TG (b, d) patterns. Curing was either at ambient (amb), or heat-cured (heat) up to 90 °C for 12 hrs. Binder was either unaltered GP cement as control (ctrl), or with elevated chemical content of 1% alkali and 4% sulfate (1N 4$). Samples were taken at 1 day (low), and day 28 (high). Major phases were identified as ettringite (*E*), portlandite (*CH*), monosulfate (*Ms*), monocarbonate (*Mc*), hemicarbonate (*Hc*), hydrogarnet (*AH₃*), and ferrite (*C₄AF*).

5   Acknowledgements

References

1.   Scrivener, K., et al., *Advances in understanding cement hydration mechanisms.* Cement and Concrete Research, 2019. **124**: p. 105823.
2.   Glasser, F.P., *The role of sulfate mineralogy and cure temperature in delayed ettringite formation.* Cement and Concrete Composites, 1996. **18**(3): p. 187-193.
3.   Ramu, Y.K., et al., *Non-deleterious delayed ettringite formation in low alkali cement mortars exposed to high-temperature steam curing.* Concrete in Australia, 2021.
4.   Shayan, A. and G.W. Quick, *Microscopic Features of Cracked and Uncracked Concrete Railway Sleepers.* ACI Materials Journal, 1992. **89**(4).
5.   MAK, J., et al. *Evaluation of Factors Pertaining to Delayed Ettringite Formation in Steam Cured Precast Concrete Members*. in *The New Zealand Concrete Industry Conference*. 2012.