

Submicroscopic Evaluation Studies to Minimize Delayed Ettringite Formation in Concrete for a Sustainable Industry and Circular Economy



Yogesh Kumar Ramu, Paul Stephen Thomas, Kirk Vessalas,
and Vute Sirivivatnanon

Abstract The high cost of maintenance, repair and retrofitting of concrete infrastructure to keep these structures durable and serviceable is not sustainable, so the design process needs to consider all aspects of deterioration mechanism/s that can potentially occur in a concrete structure. The ideal solution should contribute to sustainability by enhancing the durability of concrete elements and supporting a circular economy. We studied delayed ettringite formation (DEF), a potential deterioration mechanism, including mitigation measures, in various heat-cured cementitious systems. The results showed that continuously connected pore/crack paths at the submicroscopic level favor the transportation of DEF-causing ions in heat-cured systems. DEF increases the chance of developing cracks, which is a durability concern. To mitigate DEF, fly ash produced from an Australian bituminous coal-burning power station was incorporated in the binder to support the circular economy concept. Changes in heat-cured cementitious systems were evaluated using expansion, electrical resistivity, dynamic modulus, and microstructural studies. The pozzolanicity of fly ash was found to greatly enhance the formation of denser calcium-silica-hydrate, which in turn restricted the transportation of DEF-causing ions at the submicron level, leading to less DEF occurrence and enhancement of the durability and sustainability of concrete in field structures.

Keywords Circular economy · Delayed ettringite formation · Fly ash · Precast concrete · Sulfate attack

Y. K. Ramu (✉) · P. S. Thomas · K. Vessalas · V. Sirivivatnanon
School of Civil and Environmental Engineering, University of Technology Sydney, Ultimo, NSW,
Australia
e-mail: yogeshacct@gmail.com; yogesh.ramu@uts.edu.au

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W. Duan et al. (eds.), *Nanotechnology in Construction for Circular Economy*,
Lecture Notes in Civil Engineering 356,
https://doi.org/10.1007/978-981-99-3330-3_45

1 Introduction

Modern-day concrete infrastructure requires routine maintenance, repair and/or retrofit to ensure structures achieve their intended service life without compromising durability and sustainability. Unfortunately, the modernization of the construction industry solved a problem but created another. The precast concrete industry produces offsite concrete members to enable faster construction throughput rates for infrastructure megaprojects, but deleterious/expansive delayed ettringite formation (DEF), which has been linked to crack formation, is a significant concern for this industry [1–5]. Elevated temperature curing ($>70\text{ }^{\circ}\text{C}$) in precast concrete production is believed to be primarily responsible for inhibiting or decomposing early ettringite and, at a later stage, recrystallizing ettringite results in expansion and cracking [6]. Cracking in concrete causes permeability, which increases the risk of infiltration of external harmful agents (e.g., sulfates and chlorides) that negatively impact concrete durability. However, despite the potential risk, Australia lacks research in DEF, creating uncertainty within the industry. In this study we addressed the issue by evaluating Australian cements and their susceptibility to DEF under heat-cured conditions. The influence of sulfate and alkali spiking of these cements on DEF was also systematically studied and as mitigation of expansive/deleterious DEF, the incorporation of fly ash (FA) to enhance the durability, and thereby the sustainability of concrete, was also studied.

2 Materials and Methods

Two Australian general-purpose cements conforming to AS 3972:2010 [7] and locally sourced Gladstone FA, complying with AS 3972:2010 [8], were used. The composition of the binders was determined by X-ray fluorescence analysis (Table 1). The specific surface area of Cement 1 (C1) and Cement 2 (C2) was $395\text{ m}^2/\text{kg}$ and $420\text{ m}^2/\text{kg}$, respectively. The $\text{Na}_2\text{O}_{\text{eq}}$ content of both cements (C1: 0.5%; C2: 0.35%) complied with the Australian Technical Infrastructure Committee's specification ATIC SP-43 [9]. C1 contained 7.5% limestone as mineral addition and C2 was free from mineral addition. Modified Bogue's phase composition analysis indicated that C2 had a higher tri-calcium aluminate, C_3A (11.15%) content than C1 (7.48%). Sand sourced from Rockhampton, Queensland, was used to prepare the mortar prisms. Distilled water was used to prepare all mortar and paste specimens used in the study. Calcium sulfate and sodium hydroxide were used to chemically modify the cements.

Four different cement systems were used for mortar prisms prepared with cement:sand:water mass ratio of 1:3:0.45. Mixing of mortars was carried out according to AS2350.12-2006 [10]. Mortars were cast in steel molds (complying with AS 2350.11-2006 [11]) of size $40 \times 40 \times 160\text{ mm}$, incorporating steel expansion studs. Three prisms per mix were prepared for the expansion studies. Cement paste

Table 1 Chemical composition of binders by oxide analysis

Oxide %	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	K ₂ O	Na ₂ O	TiO ₂	LOI	Total
Cement 1 (C1)	64.2	19.7	4.8	3.1	2.4	0.9	0.4	0.2	0.2	4.1	99.9
Cement 2 (C2)	65.7	22.8	4.4	0.2	3.0	0.7	0.3	0.1	0.2	2.2	99.6
Fly ash	3.9	55.5	24.4	6.9	0.2	1.2	0.9	0.7	1.0	2.5	97.2

specimens were also prepared for characterization studies. To investigate the impact of different cement systems and heat curing on DEF, three cementitious systems and heat-curing regimes were designed: (1) cements without any additional sulfates (C1, C2); (2) cement systems with 4% sulfate and 1% alkali added (C1SN, C2-N); and (3) cement systems with 25% FA, 4% sulfate and 1% alkali added (C1SNF, C2SNF). These cement systems were used to make mortar specimens that were subjected to two different regimens (Fig. 1): ambient temperature (23 °C) cured in a humidity chamber (relative humidity (RH) 90%) for 24 h (C1-A, C2-A); heat-curing in a programmable laboratory oven. For the heat-curing process, the specimens were pre-cured at 30 °C for 4 h, followed by a temperature ramp to 90 °C, which was maintained for 12 h before natural cooling to 30 °C (\approx 6 h) (C1-H, C2-H, C1SN-H, C2SN-H, C1SNF-H, C2SNF-H). In both curing regimes, specimens were demolded 24 h after casting and transferred to a lime-saturated water bath for further curing. Changes in the length of the specimens were monitored in accordance with AS 2350.13-2006 [12], using a digital length comparator with an accuracy of 0.001 mm. The frequency of length change monitoring was every 7 days for the first 90 days, then every 30 days up to 600 days and after that, every 90 days.

For the characterization studies, the hydration of the cement pastes was arrested with solvent replacement methods at the respective ages. Hydration-arrested samples were kept in a desiccator with silica gel (as the drying agent) under laboratory-controlled conditions (23 ± 2 °C). The stored samples were tested for phase changes using Thermo gravimetric analysis. Thermal analysis was conducted with a Netzsch Jupiter F5 STA instrument using helium flowing at 40 mL/min on 20 ± 0.3 mg cement powder over a temperature range of 40–1000 °C. Dynamic modulus was calculated by the ultrasonic pulse velocity test method. Bulk electrical resistivity was evaluated by conducting electrochemical impedance spectroscopy on mortars and the results are provided in a previous study [13].

3 Results and Discussion

Figures 2 and 3 show the linear expansion trends of the cement mortar systems made with the two cements, which were exposed to ambient (23 °C) and heat-cured (90 °C) cycles as described. It can be seen that the ambient-cured mortars

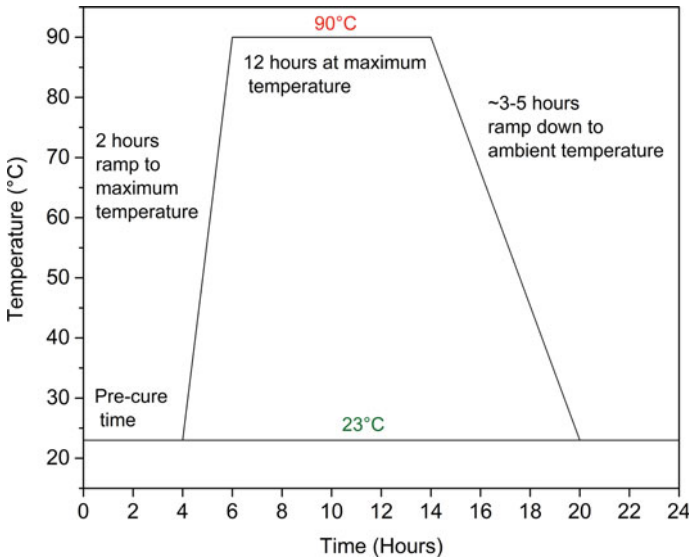


Fig. 1 Representation of ambient and heat curing regimens for cement mortars

(C1-A and C2-A) showed no expansion. Cement mortars C1-H and C2-H (in as received condition) satisfied Australian cement standards [7] and specifications [9] by showing no expansion, despite being cured at 90 °C, likely due to the lesser volume precipitation of DEF typically observed in low sulfate cements [14].

In contrast, the chemically modified cement mortars (C1SN-H, C2SN-H) containing higher levels of sulfate (4%) and alkali (1%) showed significant DEF expansion, aligning with other research studies [15, 16]. Of the chemically modified cements, C2SN-H expanded more than C1SN-H, likely because of the higher C_3A content of C2 (11.15%) compared with C1 (7.5%), which translates to higher DEF and corresponding expansion. Furthermore, from the 6 month (0.5 year) expansion data, the rate of expansion of the C2SN-H mortar was higher than the C1SN-H, also likely due to the higher quantity of C_3A , which is known to accelerate hydration reactions.

Although C1-H and C2-H did not show any significant DEF expansion, they may have formed porous hydrates because of the accelerated heat-curing regimen. The data in Table 2 support this hypothesis as the dynamic modulus and bulk resistivity values were less than those for the ambient-cured systems. This finding infers poor quality microstructure despite no observable expansion. For the highly expansive mortars, C1SN-H and C2SN-H, dynamic modulus and bulk resistivity values were found to be lower than for C1-H and C2-H, which indicated that other than the formation of porous hydrates, expansive DEF may be causing microcracks and further deteriorating the microstructure. Hence whether heat-cured cementitious systems undergo expansive DEF or not, there will be durability issues. DEF only further

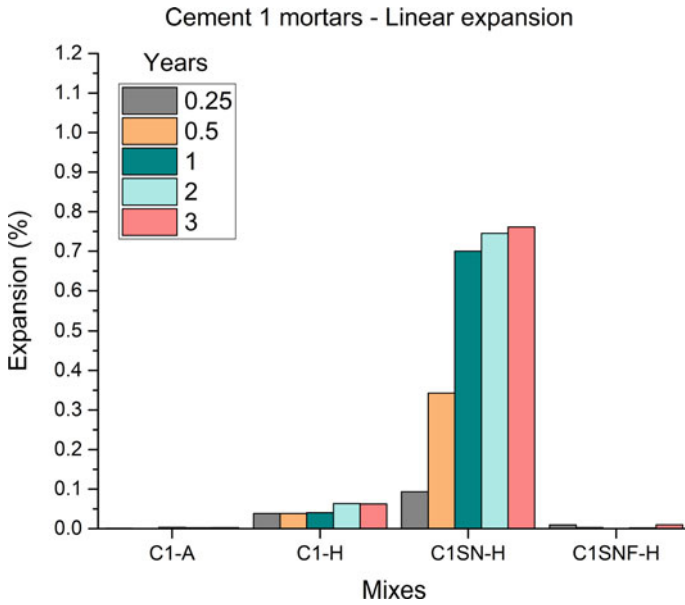


Fig. 2 Linear expansion of cement 1 mortars over 3 years

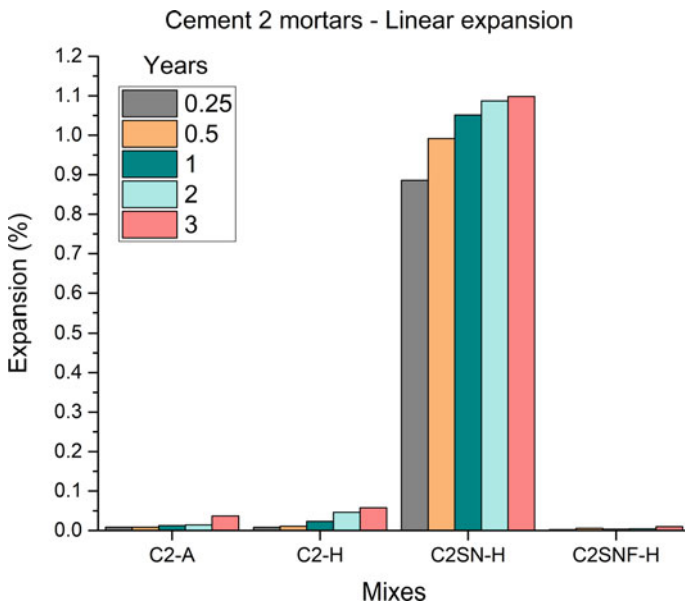


Fig. 3 Linear expansion of cement 2 mortars over 3 years

Table 2 Later-age mechanical characteristics of cement mortars

Mix	Physical characteristics at 1 year		
	Expansion (%)	Dynamic modulus (GPa)	Bulk resistivity (Ω)
C1-A	0.006	46	30
C2-A	0.015	37	22
C1-H	0.067	25	9
C2-H	0.049	26	12
C1SN-H	0.729	21	7
C2SN-H	1.058	18	7
C1SNF-H	0.001	350	51
C2SNF-H	0.003	309	40

complicates the durability issue. Therefore, the solution for DEF mitigation must also address mitigation of porous hydrates forming in these cementitious systems.

FA was included in this study to investigate its ability to mitigate expansive DEF and restrict the formation of porous hydrates. Although there has been significant research undertaken in understanding mitigation of DEF using FA [17–19], this study is unique because we tested the ability of FA to mitigate DEF in high-sulfate and high-alkali cements. As shown in Figs. 2 and 3, complete elimination of expansive DEF occurred with additional FA in both C1SNF-H, and C2SNF-H mortars despite the cement being spiked with 4% sulfate and 1% alkali. This result could be partially due to a change in the dissolution behavior of the cement, thereby reducing the overall content of aluminum and sulfate ions available in the pore solution. Thus, less ettringite would precipitate in the cementitious system. From the data in Table 2, the FA addition led to significant improvement in the dynamic modulus and bulk resistivity values, contributing to a denser and high-quality microstructure. The denser microstructure is likely due to the pozzolanicity of FA, which converts porous (10 μm –10 nm) portlandite to denser (10–0.5 nm) calcium–silica–hydrate (C–S–H). For comparison, the portlandite (calcium hydrate (CH)) content of the heat-cured cementitious systems was also studied, as shown in Fig. 4. It is evident that the portlandite content in C1SN-F was the lowest, which represents that the greater reaction of CH with reactive silica in the FA formed additional C–S–H, thus making the microstructure denser, in turn restricting the transportation of DEF-causing ions at the submicron level and eliminating any increase in deleterious DEF occurrence.

Thus, it can be deduced that incorporating FA in heat-cured cementitious systems eliminates DEF expansion and improves the microstructure by densification through the production of more gel pores and less capillary pores due to the formation of additional C–S–H. Based on our results, the following microstructural pattern (Fig. 5) is hypothesized from the circuit model proposed by Guangling [20]. The model considers concrete/mortar as a circuit when a potential difference is applied to the sample. The free transportation of ions in the pore solution is controlled by the action of continuous conductive paths. In contrast, blocked passages by the arrangement

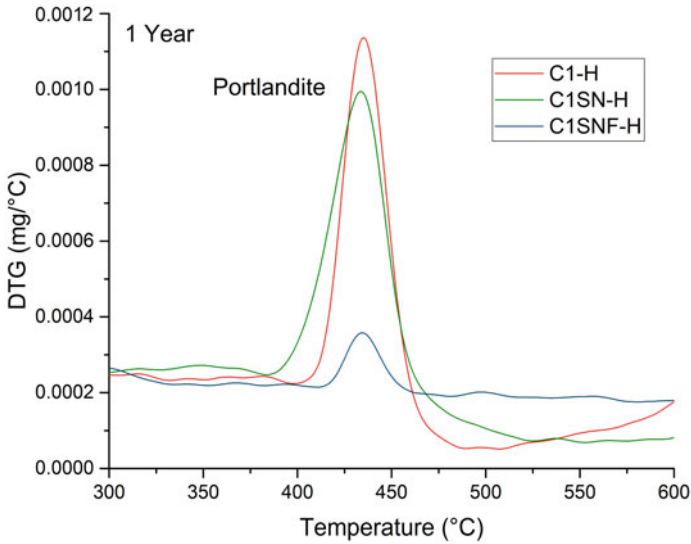


Fig. 4 Portlandite consumption of heat-cured mortars with and without fly ash

of a series of gel particles prevent the transfer of pore solution ions and are termed “insulator paths”. If some gel particles exist in the conductive paths, then points of discontinuation lead to discontinuous conductive paths. For further understanding of the concrete/mortar circuit models, please refer to Guangling [20] and Ramu et al. [13].

Figure 5a shows that the ambient-cured mortars (C1-A and C2-A) may have more insulator paths than conductive paths due to the absence of heat-induced accelerated curing, as reflected in their higher dynamic modulus and bulk resistivity values shown in Table 2. However, for the heat-cured mortars (C1-H, C2-H, C1SN-H, and C2SN-H), because of accelerated curing at 90 °C, microcracks may develop, which leads to the gel particles not being tightly arranged and giving rise to more conductive paths as represented in Fig. 5b. This scenario correlates well with the significant reduction in dynamic modulus and bulk resistivity values noted in Table 2, which creates a favorable situation whereby various ions such as Na, K, S, Ca, and Al are readily transported. Although this scenario is the same for all heat-cured mortars in our study, the C1SN-H and C2SN-H mortars contained more sulfates than C1-H and C2-H. Therefore, greater transportation and deposition of sulfur ions at different locations would increase the likelihood of DEF. Higher expansion of DEF causes expansion and microcracks, which justifies the observation from Table 2 for further reduction in dynamic modulus and bulk resistivity values.

With the incorporation of FA, greater C–S–H formation is inferred by the consumption of (CH) portlandite (Fig. 4) and this creates a pore blocking effect that leads to tightly packed gel particles creating more insulator paths, as represented in Fig. 5c. More tightly packed gel particles reduces the likelihood of ion

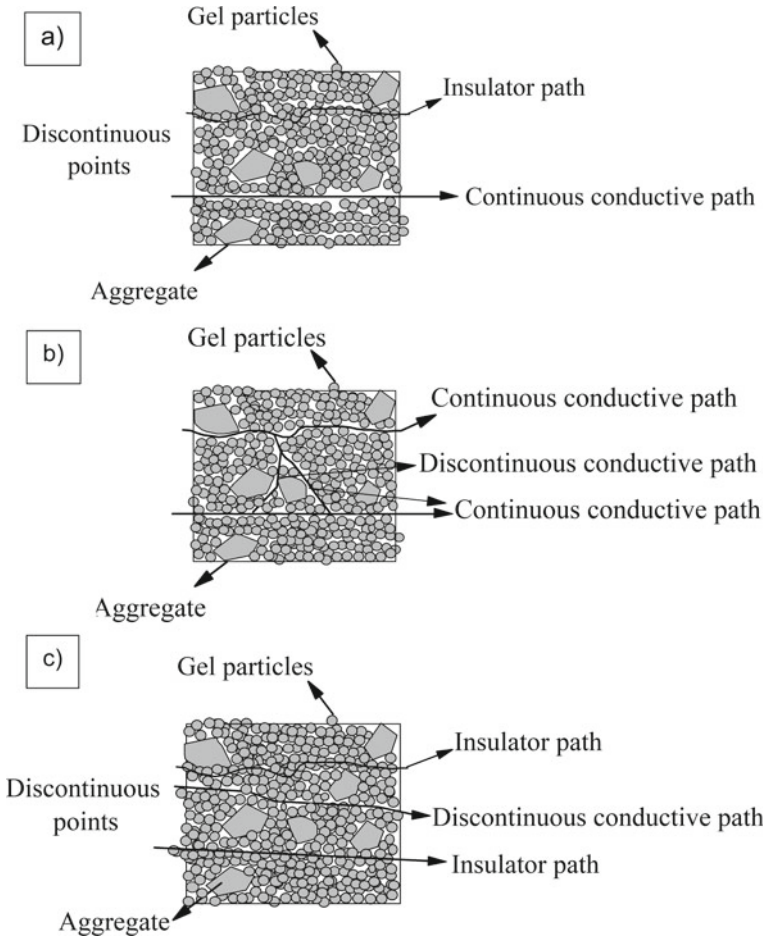


Fig. 5 Schematic representation of different mortars' microstructure (not to scale): **a** cement mortar cured at ambient temperature (25 °C) [20]; **b** cement mortar cured at 90 °C; **c** cement mortar with fly ash cured at 90 °C

transportation, thereby reducing ettringite precipitation and eliminating deleterious DEF. Thus, the incorporation of FA in heat-cured mortars has two significant benefits: (1) in highly DEF-prone cementitious systems, it can eliminate harmful expansive DEF; and (2) in non-DEF-prone cementitious systems, it can be helpful in creating a denser microstructure. Both these benefits contribute to more durable and sustainable concrete.

4 Conclusions

From this research work, the following conclusions can be made.

- (1) Cements satisfying the requirements of AS 3972:2010 [7] and ATIC SP-43 [9] for sulfate and alkali content are not prone to expansive DEF even if the concrete is heat-cured. However, due to elevated temperature curing, porous hydrates form, which leads to poor microstructural quality and eventual reduction in the durability performance of the concrete.
- (2) Chemically modified cement (sulfate 4%, alkali 1%) was prone to expansive DEF when heat-cured. A reduction in physical characteristics such as dynamic modulus and bulk resistivity was observed. Thus, if such cements are used in concrete that is heat-cured, there is a high likelihood of durability issues arising from the combined action of expansive DEF and permeability, leading to the detriment of concrete service life.
- (3) The incorporation of FA eliminated expansive DEF even in chemically modified cement mortars (sulfate 4%, alkali 1%). Furthermore, the consumption of portlandite to form additional C–S–H resulted in a much denser microstructure, as inferred from the high values for dynamic modulus and bulk resistivity. Thus, the addition of FA undoubtedly contributes to increasing the durability of heat-cured (precast) concrete, thereby also contributing to enhanced sustainability.
- (4) The conclusions presented in this study are limited to the two Australian general-purpose cements used in the research and mortar specimens. This study needs to be extended to a range of cements/clinkers and concrete specimens.

Acknowledgements We acknowledge the financial support provided by Holcim Australia and the award of a UTS international research scholarship for carrying out this research project. The Construction Materials Research Laboratory, IIT Madras, is gratefully acknowledged for laboratory support to do part of the work presented in this report.

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