Role of fly ash in mitigating durability issues due to curing cement systems at elevated temperature

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Abstract: Durability issues prevailing from curing cement at elevated temperatures are often linked to delayed ettringite formation (DEF). However, elevated temperature curing may also hinder cement from developing its key properties including long-term compressive and flexural strengths. This phenomenon is often sidelined in DEF research studies which evaluating cementitious systems and curing regimes for DEF vulnerability. Although deterioration of precast concrete elements due to expansive DEF is well documented, it should be stressed that not all DEF results in deleterious expansion. Hence the non-expansive DEF systems have the risk of being underestimated for durability concerns. In this study, cement mortar systems were prepared using two Australian cements with varying aluminate contents. These cements were chemically modified with additional sulphate and alkali to assess expansive DEF behaviour under elevated temperature curing (90°C). Expansion, electrical resistivity, and dynamic modulus were determined. Results demonstrate cementitious systems comprising high sulphate and alkali contents resulted in high DEF expansion whereas systems comprising high sulphate content resulted in non-expansive DEF only. However, even in the non-expansive DEF systems, a decrease in resistivity and dynamic modulus were noted, which is comparable to expansive DEF systems indicating microstructural damages are inevitable. Incorporating fly ash in cementitious systems significantly increased resistivity and dynamic modulus in both expansive and non-expansive DEF systems. The pozzolanic reaction and densification of the microstructure influenced the transportation properties, restricting the movement of sulphates thereby reducing ettringite precipitation. Porosity reduction due to more C-S-H formation resulted in high resistivity and modulus, thereby improving the physical characteristics of cement systems cured at higher temperature.

Keywords: Ettringite, precast concrete, DEF, steam curing, durability, specifications.

1. Introduction

In precast concrete manufacturing, concrete is mixed, formed and cast into shape, prestressed and cured in a controlled environment prior to supply and use in a construction project. The transportation, lifting and installation of prestressed and precast elements in place on a construction site requires the concrete element to have attained a requisite strength level before leaving the manufacturing facility. Reducing the concrete production time is an economic necessity for the manufacturer. Achieving 1-day strength in the range 27-31 MPa and accelerating the curing allows the precast manufacturer to release prestressing [1,2] at a much earlier age thereby helping further reduce the time required for production. Concrete strength accelerating methods in practice commonly involve the use of steam curing, autoclaving, microwave heating or electrical heating of reinforcement [3]. Although all curing methods involve curing the concrete at elevated temperatures, steam curing is accepted as the method of choice that is practiced by precast manufacturers.

The durability of steam-cured concrete in service has been questioned due to the possible occurrence of DEF. Ettringite re-precipitation, as DEF, can co-exist in both non-expansive and expansive forms. In its expansive form, DEF causes damage to concrete. Fortunately, not all forms of DEF are expansive [4]. The pre-existence of non-expansive DEF may however be misinterpreted as the leading cause of damage in concrete. As DEF studies principally rely on a fundamental understanding of expansive behaviour related to DEF occurrence, the co-existence of non-expansive DEF and its impact on the physical properties of the concrete can be easily overlooked.

In this investigation, both expansive and non-expansive heat-cured systems have been studied in detail to assess and correlate the durability behaviours of both systems. Further, the role and the ability of fly ash to be used as supplementary cementitious material addition for the partial replacement of cement in mortar to mitigate expansive DEF and other durability concerns has been studied.

2. Materials

Two Australian general purpose (GP) cements conforming to AS 3972: 2010 [5] and a locally sourced fly ash conforming to AS 3582.1: 2016 [6] were used in this study. The composition of the binders was determined using X-ray Fluorescence (XRF) analysis and the results are given in Table 1. The specific surface area of Cement 1 (C1) and Cement 2 (C2) is 395 m^2/kg and 420 m^2/kg, respectively. The Na_2O_{eq} contents of both cements (C1- 0.5%; C2- 0.35%) complies with Australian Technical Infrastructure Committee's specification ATIC SP-43 [7]. Modified Bogue's phase composition analysis indicates that C2 has a higher tri-calcium aluminate C_3A (11.15%) content compared to C1 (7.48%). Two sands, a fine and coarse sand, were used to prepare the mortar prisms. These aggregates were both sourced from Rockhampton, Queensland. Analytical grade gypsum and sodium hydroxide were used to change the chemistry of cement. Distilled water was used for preparing the mortar specimens throughout the study.

Table 1. Chemical composition of binders by oxide analysis (XRF)

Oxide %	Cement 1 (C1)	Cement 2 (C2)	Fly ash (FA)
CaO	64.18	65.70	3.88
SiO_2	19.67	22.82	55.46
Al_2O_3	4.78	4.38	24.42
Fe_2O_3	3.10	0.26	6.91
SO_3	2.37	3.07	0.19
MgO	0.91	0.68	1.22
K2O	0.41	0.29	0.88
TiO_2	0.22	0.26	1.05
Na_2O	0.23	0.16	0.77
P_2O_5	0.06	0.07	1.14
Mn_2O_3	0.12	0.02	0.04
LOI	4.09	2.20	2.52
Total	100.14	99.91	98.48
Na_2O_{eq}	**0.50**	**0.35**	**NA**

3. Experimental program

To generate expansive DEF in laboratory mortar specimens, the chemistry of cements was modified to include 4% sulphate (C1-S and C2-S) without altering the alkali content and to also include 4% sulphate and 1% alkali (C1-SN and C2-SN). Control mortar specimens were made using the 'as received' cements (C1 and C2) without any chemistry modification. Further to study the impact of fly ash addition in mitigating durability issues in heat-cured cementitious systems, 25% of cement was replaced with fly ash in C1-SN and C2-SN mortars. Curing concrete at elevated temperature is another essential factor required for DEF. Mortar systems assessed in the study were subjected to a higher curing temperature than the specification limit imposed by precast concrete manufacturers in Australia (75°C). A curing regime of 90°C for 12 hours after 4 hours of pre-cure time (Figure 1) was employed to encourage DEF. To perform this temperature steam-curing regime a laboratory programmable oven was used to hold and ramp up and down temperature cycles. A standard 23°C curing regime was also employed to simulate standard concrete curing conditions. For both curing regimes, specimens were demoulded after 25 hours and transferred to lime-saturated water for further storage.

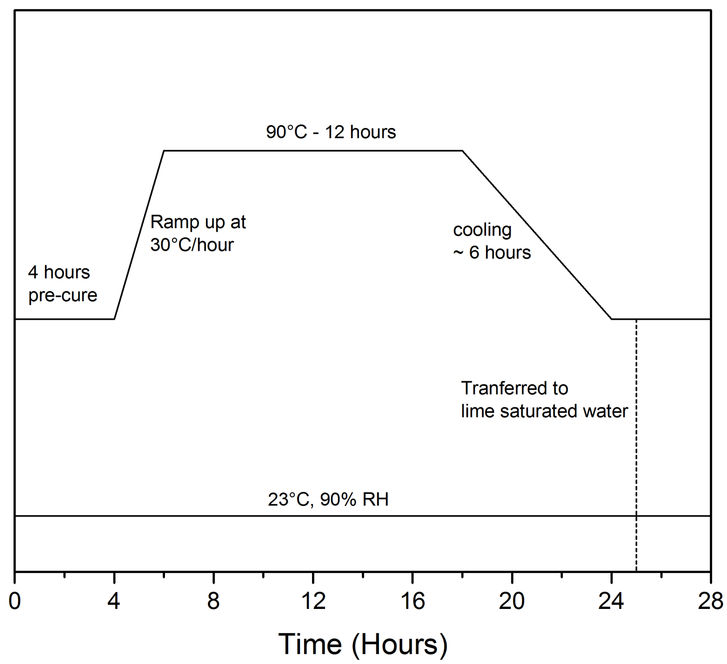

Figure 1. Curing regimes imposed on cement mortars

4. Experimental methods

Mortar prisms were prepared using a cement/coarse sand/fine sand/water mass ratios of 1:2.5:0.5:0.45. The mixing of mortars was carried out according to the requirements given in AS 2350.12-2006 [8]. Mortars were cast in steel moulds (complying with AS 2350.11-2006 [9]) of size 40 x 40 x 160 mm comprising steel expansion gauge studs. Three prisms per mix were prepared for the expansion studies. A fourth specimen was also prepared for characterization studies.

The length change of specimens were monitored in accordance with the procedure given in AS 2350.13-2006 [10] using a digital length comparator with an accuracy of 0.001 mm. An initial length reading was taken after 7 days of curing. The frequency of length change monitoring was carried out every 7 days for the first 90 days, then once every 90 days for up to 1050 days. To obtain an insight into the microstructural features of mortar specimens that experienced DEF, electrical surface resistivity measurements were also conducted on select mortar prisms using a four-point Wenner probe at the specimen age of 500 days. For consistency, all the surface resistivity measurements were carried out on the specimens in a dampened condition. Further, the dynamic modulus was determined indirectly from the ultrasonic pulse velocity method, using the equation (1)

$$E_d = \frac{\rho V^2 (1 + \mu_{pr})(1 - 2\mu_{pr})}{(1 - \mu_{pr})} \quad (1)$$

where Ed is the dynamic modulus of elasticity in GPa, ρ is the density of mortar in Kgm^3, V is pulse velocity in km/s and μ_{pr} is the dynamic Poisson's ratio of concrete. Density is measured from the product of mass and volume of the sample and Poisson's ratio is assumed with an average value of 0.24 [11,12].
Furthermore, DEF precipitation in specimens was studied by backscatter electron BSE-SEM imaging. Mortar prisms were thin sectioned to have a thickness around 5 mm and hydration was arrested by solvent exchange using isopropanol [13]. Hydration arrested specimens were resin-impregnated using a mixture of low viscous epoxy resin and hardener under vacuum [14]. Specimens were then polished and coated with Au-Pd to a thickness of about 9-10 nm under vacuum. A Carl ZEISS EVO scanning electron microscope (SEM) was used for the microstructural studies.

5. Results and discussion

The expansion results of mortar prisms are shown in Figure 2. The results show that there was no significant DEF expansion for the heat-cured mortars made with the C1 and C2 cements at 90°C in their as-received condition. Importantly, the expansion observed at 90°C was similar to that observed for the control mortar prisms at 23°C. This observation is likely due to the low sulphate and alkali levels found in the C1 and C2 cements (Table 1) when compared with published data for cements used in other studies [4,14].

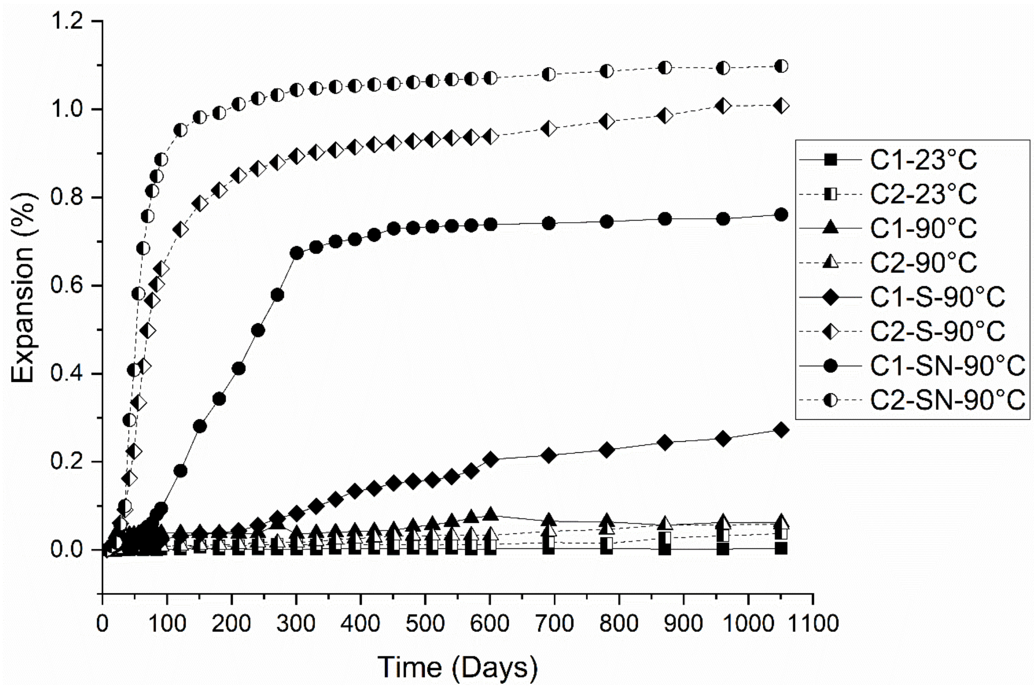

Figure 2. Expansion of mortar prisms cured at 23°C and 90°C

Upon increasing the sulphate and alkali contents, the significance of curing at the elevated temperature (90°C) became apparent. Significant expansions were observed indicating the high likelihood of the presence of expansive DEF. Further, the expansion was noted to be relatively high for the sulphate (4%) and alkali (1%) cement mortars when compared to sulphate (4%) alone cement mortars. This signifies the role of higher temperature increasing the solubility of sulphate in pore solution due to the presence of increased alkali [15]. Furthermore, mortars made with C2 cement which had 11.5% C_3A expanded more than the C1 mortars that had 7.48% C_3A, likely due to the higher alumina content of C2 cement most likely also contributing to increased precipitation of ettringite [16].

To confirm the expansion that had resulted was due to DEF occurrence, the microstructure of representative C1 mortar specimens were also studied (Figure 3). From Figure 3.a, b, it is observed that the C1 specimens cured at 23°C and 90°C were absent of ettringite precipitation at both the interfacial transition zone (ITZ) and within the cement paste regions corelating well with the expansion results. In contrast, a band of distinct ettringite precipitation was found in the C1-SN-90°C specimens at the ITZ suggesting the presence of expansive DEF (Figure 3.c). The confirmed presence of expansive DEF correlates well with the expansion results in these mortars.

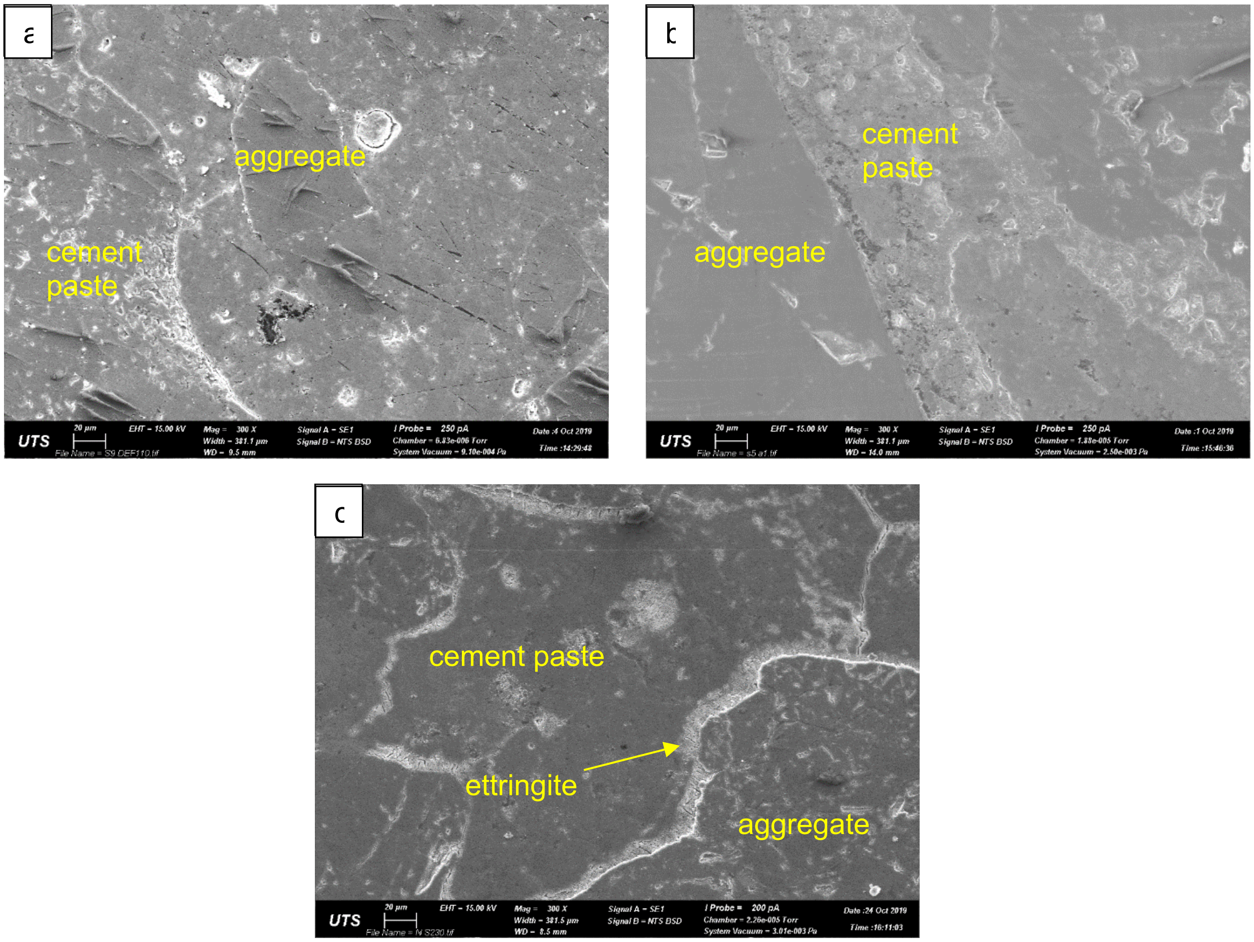

Figure 3. Micrographs showing a) control specimen cured at 23°C b) control specimen heat-cured at 90°C c) spiked specimen with 4% sulphate and 1% alkali heat-cured at 90°C (500 days) (300 X)

The electrical resistivity and dynamic modulus of mortar specimens were also determined after 500 days (Figure 4). A significant drop in electrical resistivity and dynamic modulus was evident in both C1-90°C and C2-90°C mortars despite being non-expansive. The reduction in electrical resistivity suggests that the mortar permeability had increased owing to the formation of coarse hydrates during elevated temperature curing [17]. Further, the noted reduction in dynamic modulus might infer the overall physical characteristics of the mortar had been compromised due the presence of more a permeable matrix [18]. In the case of sulphate and sulphate and alkali spiked cement mortars (C1-S-90°C, C2-S-90°C, C1-SN-90°C and C2-SN-90°C), the resistivity and dynamic modulus data were observed to reduce further owing to the combined effect of coarse hydrates formation and expansive DEF precipitation presence [19].

With the non-expansive nature and absence of ettringite in non-sulphate and alkali modified systems (C1-90°C and C2-90°C), the likelihood of expansive DEF occurring in heat-curing regimes followed in this study appears low. However, the results from electrical resistivity and dynamic modulus suggest microstructural damage may result possibly due to other thermal effects [20], which could impact the durability. Hence, there is a need to achieve both non-expansive and impermeable heat-cured systems to avoid any potential durability concerns, thus guidelines for reducing the risk of cracking due to thermal effects need to be followed.

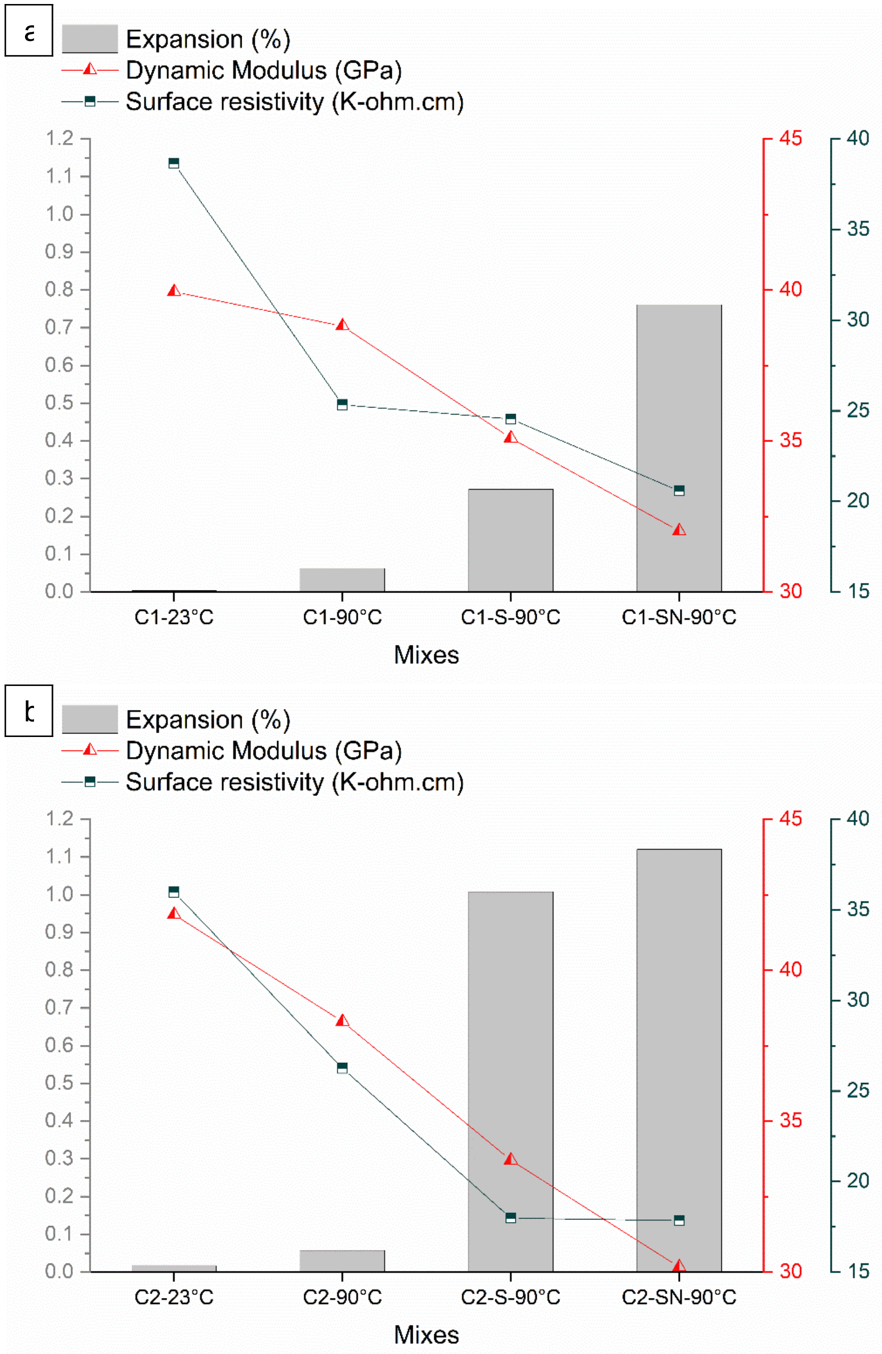

Figure 4. Changes in dynamic modulus and electrical resistivity (500 days) in a) C1 mortars b) C2 mortars compared with absolute expansion (1050 days)

Fly ash incorporation in the highly expansive chemically modified systems (4% sulphate and 1% alkali) resulted in complete elimination of expansion (C1-SN-FA-90°C and C2-SN-FA-90°C) as shown in Figure 5. Further, the addition of fly ash was found to significantly increase the dynamic modulus and electrical resistivity of the specimens studied. DEF precipitation and microcracks were observed to be absent in the microstructural studies that were carried out on these mortars (Figure 6). Thus, the mitigation of expansive DEF and the improvement noted in physical characteristics are aligned well with the use of fly ash despite the specimens cured at 90°C for 12 hours [18,21]. A reason for this improvement may be due to the pozzolanic reaction of fly ash and portlandite (calcium hydroxide) to form additional denser calcium silicate hydrate (C-S-H), which also results in pore refinement [22]. Pore refinement has the added advantage of restricting the transport of ions [23], which may have prevented sulphate and alumina ions from permeating through the microstructure and reacting with calcium ions to form ettringite. This results in reducing the risk of DEF by increasing the impermeability (as reflected by the resistivity data) of the microstructure leading to the increase in resistivity and dynamic modulus of this system when compared with others investigated in this study.

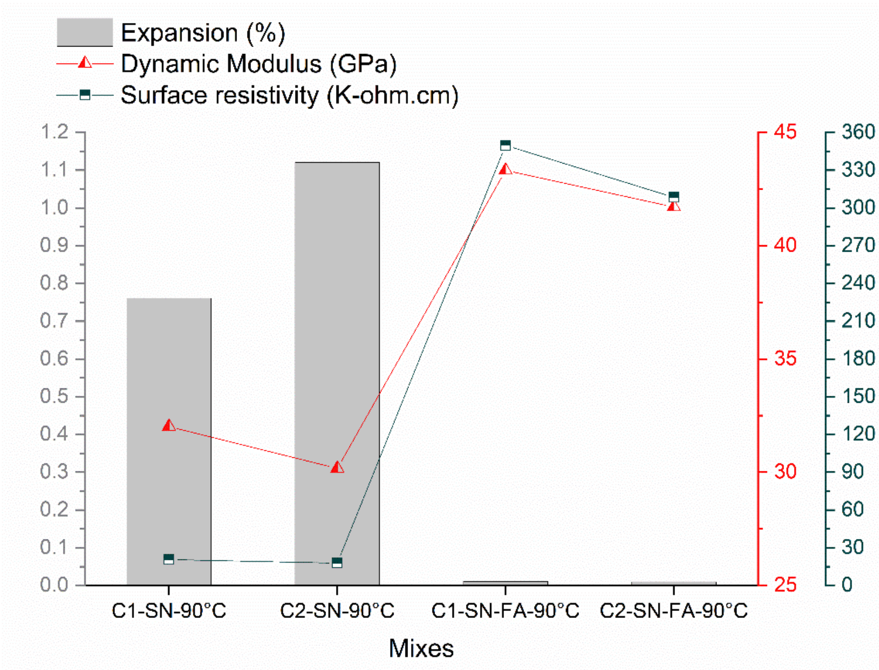

Figure 5. Impact of incorporating fly ash and changes in dynamic modulus and electrical resistivity (500 days) in C1 and C2 mortars incorporating 4% sulphate and 4% sulphate and 1% alkali compared with absolute expansion (1050 days)

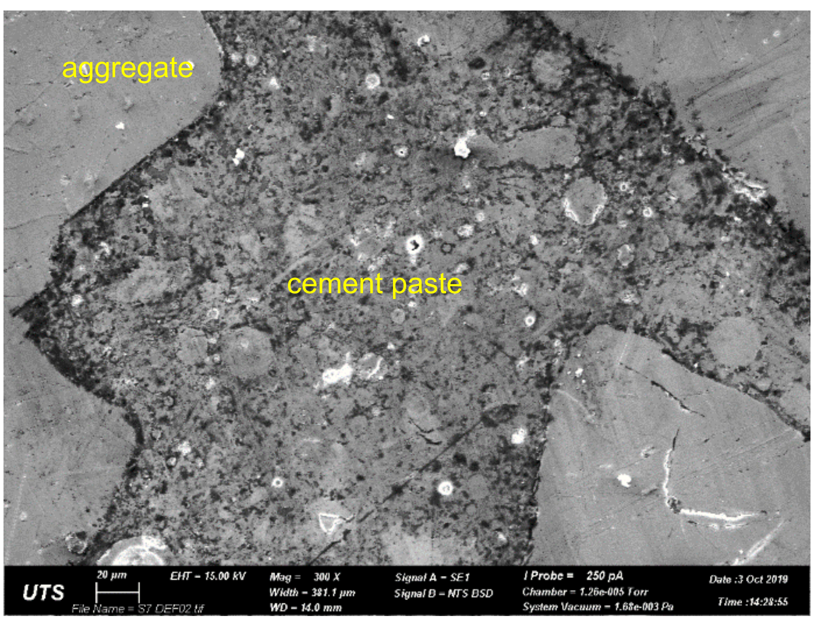

Figure 6. Micrograph showing fly ash specimen heat-cured at 90°C (500 days) (300 X)

6. Conclusions

From this study, the following conclusions can be drawn.

1. Mortar specimens heat cured at 90°C for 12 hours and prepared using commercial Australian cements with alkali and sulphate contents within standard specification (Na_2O_e < 0.6%; SO_3 < 3.5%) were not observed to expand due to DEF precipitation.

2. The lack of expansion suggests that DEF is unlikely to be observed for steam cured precast concrete members manufactured using commercial Australian cements. The results of this study suggest that the risk of expansive DEF may be mitigated by controlling the cement sulphate or alkali content.

3. Structural degradation of the microstructure of heat cured mortars was observed by resistivity and dynamic modulus measurements. Guidelines used for managing thermal effects in concrete to limit cracking need to be followed.

4. Use of fly ash in heat-cured cementitious systems (90°C) was found to eliminate the presence of expansive DEF. The microstructure of such mortars was found to be more impermeable, likely by pore refinement due to the pozzolanic reactions.

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8. References

[1] R.. Day, The effect of secondary ettringite formation on the durability of concrete: A literature analaysis, 1992.

[2] O.A. EL-Zein, High early strength concrete studies, Masters thesis, University of Windsor, Ontario, 1973. https://doi.org/10.16953/deusbed.74839.

[3] A.A. Ramezanianpour, M.H. Khazali, P. Vosoughi, Effect of steam curing cycles on strength and durability of SCC: A case study in precast concrete, Constr. Build. Mater. 49 (2013) 807–813. https://doi.org/10.1016/j.conbuildmat.2013.08.040.

[4] K.L. Scrivener, D. Damidot, C. Famy, Possible Mechanisms of Expansion of Concrete Exposed to Elevated Temperatures During Curing (Also Known as DEF) and Implications for Avoidance of Field Problems, Cem. , Concr. Aggregates. 21 (1999) 93–101.

[5] Australian Standard: General purpose and blended cements (AS 3972-2010), 2010.

[6] Australian Standard: Supplementary cementitious materials Part 1 : Fly ash (AS 3582.1:2016), 2016.

[7] Australian Technical Infrastructure Committee: Cementitious materials for concrete (ATIC SP-43), 2017.

[8] Australian Standard: Methods of testing portland, blended and masonry cements Method 12: Preparation of a standard mortar and moulding of specimens (AS 2350.12—2006), 2006.

[9] Australian Standard: Methods of testing portland, blended and masonry cements Method 11: Compressive strength (AS 2350.11:2006), 2006.

[10] Australian Standard: Methods of testing portland, blended and masonry cements Method 13: Determination of drying shrinkage of cement mortars (AS 2350.13—2006), 2006.

[11] IS: 13311(Part I), IS: 13311 (Part I) , Non-destructive testing of concrete methods of test

(Ultrasonic pulse velocity), Bureau of Indian Standard, 1992.

[12] A.K. Chandrappa, K.P. Biligiri, Influence of mix parameters on pore properties and modulus of pervious concrete: an application of ultrasonic pulse velocity, Mater. Struct. Constr. 49 (2016) 5255–5271. https://doi.org/10.1617/s11527-016-0858-9.

[13] R. Snellings, J. Chwast, Ö. Cizer, N. De Belie, Y. Dhandapani, P. Durdzinski, J. Elsen, J. Haufe, D. Hooton, C. Patapy, M. Santhanam, K. Scrivener, D. Snoeck, L. Steger, S. Tongbo, A. Vollpracht, F. Winnefeld, B. Lothenbach, Report of TC 238-SCM: hydration stoppage methods for phase assemblage studies of blended cements—results of a round robin test, Mater. Struct. Constr. 51 (2018). https://doi.org/10.1617/s11527-018-1237-5.

[14] K. Scrivener, R. Snellings, B. Lothenbach, A Practical Guide to Microstructural Analysis of Cementitious Materials, Taylor & Francis, 2016. https://books.google.com.au/books?id=X2t6rgEACAAJ.

[15] M.D.A. Thomas, R.D. Hooton, T. Ramlochan, Use of pore solution analysis in design for concrete durability, Adv. Cem. Res. 22 (2010) 203–210. https://doi.org/10.1680/adcr.2010.22.4.203.

[16] Z. Zhang, J. Olek, S. Diamond, Studies on delayed ettringite formation in heat-cured mortars II . Characteristics of cement that may be susceptible to DEF, Cem. Concr. Res. 32 (2002) 1737–1742.

[17] E. Gallucci, X. Zhang, K.L. Scrivener, Effect of temperature on the microstructure of calcium silicate hydrate (C-S-H), Cem. Concr. Res. 53 (2013) 185–195. https://doi.org/10.1016/j.cemconres.2013.06.008.

[18] N. Leklou, V.H. Nguyen, P. Mounanga, The effect of the partial cement substitution with fly ash on Delayed Ettringite Formation in heat-cured mortars, KSCE J. Civ. Eng. 21 (2017) 1359–1366. https://doi.org/10.1007/s12205-016-0778-9.

[19] Z. Zhang, J. Olek, S. Diamond, Studies on delayed ettringite formation in early-age , heat-cured mortars I . Expansion measurements , changes in dynamic modulus of elasticity , and weight gains, Cem. Concr. Compos. 32 (2002) 1729–1736.

[20] Y. Dhandapani, M. Santhanam, Assessment of pore structure evolution in the limestone calcined clay cementitious system and its implications for performance, Cem. Concr. Compos. 84 (2017) 36–47. https://doi.org/10.1016/j.cemconcomp.2017.08.012.

[21] S. Zhuang, J. Sun, The feasibility of properly raising temperature for preparing high-volume fly ash or slag steam-cured concrete: An evaluation on DEF, 4-year strength and durability, Constr. Build. Mater. 242 (2020) 118094. https://doi.org/10.1016/j.conbuildmat.2020.118094.

[22] D.C. Hughes, Sulphate resistance of OPC, OPC/fly ash and SRPC pastes: pore structure and permeability, Cem. Concr. Res. 15 (1985) 1003–1012. https://doi.org/10.1016/0008-8846(85)90091-2.

[23] Y. Dhandapani, K.L. Scrivener, M. Santhanam, Temperature Effects on Performance of Cementitious Systems : Microstructure and Transport Properties, in: 71st RILEM Annu. Week ICACMS 2017, Chennai, India, 2017: pp. 1–10.