Article

Assessment of the Potential for Delayed Ettringite Formation in Heat Cured Mortars and Concrete Using Australian Materials

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Abstract: Delayed ettringite formation (DEF) is a recognised durability issue in concretes where the temperature during curing has been elevated. To address the potential risk of DEF, Australian specifications for heat and steam cured concretes, such as TfNSW B80, MRTS 70, and MRS 820, restrict the maximum concrete temperature during heat or steam curing to 70 or 80 °C (depending on the jurisdiction). The wide range of road authority specifications in Australia has led to uncertainty among precast concrete manufacturers, designers, and contractors, as there is a lack of clarity on how less durable the concretes become when they breach these temperature limits. Moreover, the role of supplementary cementitious materials (SCMs) in mitigating DEF in the specifications is unclear. This paper addresses these concerns by reporting some of the outcomes from research carried out over the last 8 years at the University of Technology Sydney investigating the factors that raise the risk of deleterious DEF. The work indicates that the risk of DEF is low if the cements conform to Australian specifications (AS 3972 and ATIC-SP43). The risk is further reduced if fly ash (FA) is used as part of the binder composition. As the risk of DEF is low if a limit is placed on the alkali and sulphate contents in the cement and is further mitigated if FA is used to partially replace the cement, a more practical and standardised approach to heat cured concrete specifications across the Australian jurisdictions could be adopted.

Keywords: delayed ettringite formation (DEF); precast concrete; SO_3; Na_2O_e; heat curing; mortar; concrete

1. Introduction

Delayed ettringite formation (DEF) is a potentially deleterious reaction which occurs in concrete when the curing temperature of the concrete exceeds the elevated temperature threshold [1–4]. The source of the elevated temperature may be mass pours or during heat or steam curing of precast elements. The issue is the decomposition or inhibition of early age ettringite through elevation of the temperature during curing in the plastic phase at early age followed by reprecipitation of ettringite at a later age once the concrete has hardened. As ettringite is an expansive phase, stresses developed during the delayed reformation of ettringite may result in expansion and cracking of the concrete.

A number of critical factors are necessary for DEF to occur and are based around the decomposition of formed or the inhibition of the formation of early ettringite in the plastic phase of the concrete. These are [5,6]:

1. Duration of the precure time prior to the heat cure cycle—typically 4 h is used as the length of the precure, however, in laboratory experiments shorter precure times have exacerbated expansion associated with DEF; longer precure times reduce the risk of DEF.

2. Temperature and duration of the curing cycle—70 °C is a widely reported threshold temperature, although some data have been reported suggesting the observation of DEF at lower curing temperatures; increasing the duration of the heat curing cycle also increases the risk. Higher temperatures (>90 °C) and longer heat cure cycles (>10 h) result in significantly greater risk of expansion associated with DEF and have been the focus of much of the laboratory research.

3. Moisture—a relative humidity of >90% is required [7]. The precipitation of ettringite and the transport of sulphate ions in the concrete occurs through the pore solution. Generally, DEF is not observed for concretes which are dry.

4. Calcium aluminate (C_3A) content—DEF occurs for a C_3A content >7%, although DEF has also been observed for C_3A contents as low as 5%. As C_3A is a reactant in the formation of sulphoaluminates such as ettringite, C_3A is required in reasonable proportions for DEF.

5. Sulphate content (represented by SO_3)—DEF occurs for a SO_3 content >3%. Similarly, sulphate is a reactant in the precipitation of ettringite.

6. Sulphur trioxide to aluminium oxide molar ratio ($[SO_3]/[Al_2O_3]$)—DEF is at its pessimum when the $[SO_3]/[Al_2O_3] \approx 1.1$.

7. Alkali content—elevated alkali contents in the pore solution promotes DEF. The presence of alkali (Na^+, K^+) ions in the pore solution increase the solubility of sulphate ions leading to the decomposition of early ettringite. Leaching of alkali content at a later stage, in the hardened state, is also responsible for accelerating DEF.

These are the major factors associated with DEF occurrence, although other factors such as cement fineness, water-binder ratio (w/b), restraint, pore size distribution and aggregate characteristics may also have an influence on DEF [7–14]. To understand why these factors are important, it is necessary to first discuss the role of ettringite and its stability during the curing phase of the concrete.

Ettringite (a calcium sulphoaluminate, AF_t ($C_6A\$_3H_{32}$)) is usually formed in the plastic state of concrete (early ettringite formation (EEF)). Although ettringite is an expansive phase, precipitation of early ettringite in the plastic state is not a significant issue as the increased volume can be easily accommodated. Indeed, gypsum (calcium sulphate dihydrate ($C\$H_2$)) is interground with clinker in the manufacture of cement to promote the formation of EEF to inhibit flash set caused by the rapid hydration of the C_3A present [15].

$$C_3A + 3C\$ + 32H \rightarrow C_6A\$_3H_{32} \tag{1}$$
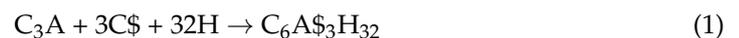
If, however, the concrete temperature experienced during curing exceeds a designated threshold temperature, a threshold temperature of 70 or 80 °C is commonly identified (e.g., Australian State specifications, TfNSW B80, MRTS 70, and MRS 820 [16–18]), the ettringite formed in the early stages of hydration is decomposed and the further formation of ettringite during the plastic stage is inhibited. Elevated temperatures can result from the combination of external heating, such as occurs in heat or steam curing, and through the exothermic hydration reactions occurring in the cement, particularly in large elements where the concrete acts as a thermal insulator resulting in elevated core temperatures [1].

Ettringite is formed when the solution is saturated with sulphate ions. The decomposition of ettringite during the heat curing cycle is related to the change in solubility of sulphate ions during the heating cycle [19–24]. The solubility limit for sulphate ions is also strongly influenced by the alkalinity of the pore solution and the temperature of the concrete [19]. Raising the temperature of the pore solution in the presence of alkali leads to the decomposition of the ettringite and the formation of calcium monosulphoaluminate (AF_m, $C_4A\$H_{12}$) according to the relationship:

$$C_6A\$_3H_{32} \rightleftharpoons C_4A\$H_{12} + 2C\$ + 20H \tag{2}$$
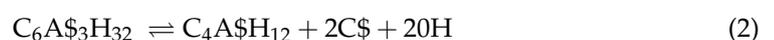
After the heat curing cycle, the temperature of the concrete is allowed to return to ambient temperature. At the lower ambient temperature, the sulphate solubility is signif-

icantly reduced and saturation of the pore solution with respect to sulphate ions occurs. Under these conditions, sulphoaluminates may reprecipitate and ettringite can slowly recrystallise, but this time the recrystallisation of ettringite is in the concrete's hardened state where the expansion can no longer be accommodated. If the volumetric stresses induced by this expansion are exceeded, cracking will occur undermining the serviceability of the concrete [9,25–28]. Cracking induced by deleterious DEF has been observed for mass pours such as in abutments, piers and dams or for heat cured precast concretes [1,29].

The factors outlined above (precure time, maximum curing temperature, alkali, sulphate, and aluminate content), are required in combination in order to increase the risk of DEF [6,21]. Accordingly, addressing these factors can also reduce or eliminate the risk of DEF. As such, Australian state road and traffic authorities have defined limits for the maximum curing and concrete temperatures. These limits are summarised in Table 1. The typical limit imposed for heat or steam cured concrete is 70 °C, although Queensland TMR and South Australia DIT/DPTI specifications allow for a maximum of circa 80 °C provided that GP blended cement is used. The low limit of 70 °C is difficult to achieve in steam cured concretes due to the contribution of the heat of hydration of the cement to the temperature rise, in particular mass pours, where temperatures greater than 70 °C may be reached [30]. Additionally, the limits used are derived from DEF studies conducted in other jurisdictions, where either the sulphate or alkalis contents, or both, are not strictly regulated (allowable cement sulphate and alkali contents in various countries' standards and their correlation with field case DEF have been reviewed elsewhere [31]). Australian commercial cements, on the other hand, comply with Australian Standard AS 3972-2010 [32] and Australian Technical Infrastructure Committee (ATIC) Specifications SP43 which restrict sulphate content to 3.5% SO_3 (although a specified limit of 3.0% may be preferable, c.f. TfNSW B80) and the alkali content to 0.6% Na_2O_e ($=\%Na_2O + 0.658 \times \%K_2O$). Given the tight specification in compositional limits of Australian GP cements, the strict limits of concrete temperature for steam or heat cured elements in Australia may be overly conservative. This study, therefore, sets out to identify the potential for deleterious DEF in both mortars and concretes using standard specification Australian cements (AS 3972-2010 and ATIC SP-43 [32,33]). The paper reports the expansion in mortar and concrete specimens manufactured using as received AS 3972 conforming cements, as well as cements modified to be non-conforming with elevated alkali and sulphate contents, by heat curing mortar and concrete specimens at 90 °C for 12 h to replicate the curing environment observed in the temperature profiles measured in manufactured precast elements [34].

Table 1. List of temperature limits defined by Australian standards and state road and traffic authority specifications Australia wide. Note that, in Australia, alkali limits are specified by ATIC SP43 for cement at 0.6% Na_2O_e and by AS HB79 at 2.8 kg/m^3 Na_2O_e and the cement sulphate content is limited by AS 3972 at 3.5% SO_3.

State	Road Authority Specification	Steam Curing Temperature Conditions
Australia	Standards Australia, AS 5100.5 Clause 4.11 [35]	Concrete temperature ≤ 75 °C except where analysis has been performed that justifies a particular maximum temperature for the concrete.
Australia	Standards Australia, AS 1597.2 2013, Clause Appendix C5.3 maximum temperature [36]	The maximum enclosure temperature shall be ≤70 °C. No mention of concrete temperature.
New South Wales	Transport for NSW QA Specification B80 Concrete Work for Bridges, 2021 Clause: 7.12.4 [16]	Maximum temperature of the concrete ≤ 70 °C
Queensland	Transport and Main Roads Specifications MRTS70 Concrete, 2022 Clause: 16.7.4 [17]	The enclosure temperature must be ≤70 °C. Core concrete temperature must be ≤80 °C.
South Australia	Structures—Master Specification ST-SC-S4 Low Pressure Steam Curing of Precast Units Clause 5.3 DPTI: Design Standards Structural 2015 Clause 6.2.1(e) [37]	The enclosure temperature must be ≤70 °C. Concrete temperature ≤ 82 °C
Victoria/Tasmania	VicRoads Specification 2020 Clause 610.24(g) [38]	The enclosure temperature must be ≤70 °C. Concrete temperature must be ≤75 °C.
Western Australia	Concrete for Structures—Main Roads Specification 820, 2023 Clause: 820.71 [18]	The curing temperature must be ≤70 °C

2. Materials and Methods

The materials used in this study to produce the mortars and concretes were standard commercial locally available raw materials (cement, fly ash, coarse, and fine aggregates). To investigate the role of the C_3A content of the GP cement, two standard general purpose (GP) cements were used to make mortar and concrete prisms in each experimental program. For the mortar prisms grey (GP-M) and off-white (OW-M) cements were used; similarly, for the concrete prisms grey (GP-C) and off-white (OW-C) cements were used. As the mortar and concrete experimental programs were carried out at different times, different cements, FA, and aggregates were used. The oxide compositions for the cements and the FAs used in this study are listed in Table 2. For both the mortars and concretes the fine and coarse aggregates conformed to the gradings defined by AS 2758.1 [39]. The fine aggregates were sub 4.75 mm in particle size and for the concretes a blend of 20 mm and 10 mm aggregates were used in a 3 to 1 ratio in addition to the fine aggregate.

Table 2. Chemical composition of the cements and FAs determined by XRF. The cements are designated GP—general purpose cement and OW—off-white cement. The cement and FA used in mortars are designated M and in concrete, C.

Oxide%	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	MgO	K$_2$O	Na$_2$O	LOI	Total	Na$_2$O$_e$
GP-M	64.2	19.7	4.8	3.1	2.4	0.9	0.4	0.2	4.1	99.9	0.46
OW-M	65.7	22.8	4.4	0.2	3.0	0.7	0.3	0.1	2.2	99.6	0.30
FA-M	3.88	55.46	24.42	6.91	0.19	1.22	0.77	0.88	2.52	98.7	N/A
GP-C	64.1	19.4	4.9	3.0	2.6	1.2	0.45	0.17	4.0	100.1	0.47
OW-C	65.1	20.2	5.4	0.7	3.2	1.2	0.42	0.07	3.8	100.4	0.35
FA-C	3.6	58	26.3	7.2	0.2	1.1	0.84	0.3	0.9	100.4	N/A

N/A—not applicable

Using a modified Bogue's method, the phase composition of the GP cements was calculated from the oxide content. These phase compositions are listed in Table 3. The compositions of the GP-M and GP-C cements are very consistent; however, the compositions of the OW-M and OW-C cements vary with respect to C_3A content which influences the potential for DEF induced expansion.

Table 3. Modified Bogue's phase composition of cements.

Compound	GP-M	OW-M	GP-C	OW-C
C$_3$S%	49.9	56.3	52.7	48.6
C$_2$S%	18.3	22.9	15.9	21.2
C$_3$A%	7.4	11.2	7.9	13.1
C$_4$AF%	9.4	0.8	9.1	2.1

To develop expansion in the mortar and concrete prisms due to DEF, a pessimum composition, the composition expected to result in the greatest degree of DEF induced expansion, was introduced raising the alkali and sulphate contents of the GP cements to 1% Na$_2$O$_e$ and 4% SO$_3$ by mass using laboratory grade NaOH and CaSO$_4$·2H$_2$O. This composition was used to promote ettringite precipitation; these mixes are designated 1N4$. Sulphate addition was carried out by adding laboratory grade CaSO$_4$·2H$_2$O powder to the dry ingredients prior to adding the mixing water; alkali addition was carried out by preparing a solution with the required amount of sodium hydroxide in the mixing water for the mortars and in part of the mixing water for the concretes.

FA was used as the supplementary cementitious material (SCM) in partial substitution of the GP cement at 25% by mass in both the mortar and the concrete prisms. Mortar and concrete containing FA are designated as such.

The fine aggregate used in the mortar prism tests was an alkali-silica reaction (ASR) non-reactive (NR) aggregate. For the concrete prisms, two coarse aggregates were used; an

ASR non-reactive (NR) basalt and an ASR reactive (R) dacite; the fine aggregate used was non-reactive.

Although two curing processes, ambient cured and heat cured, were used for both mortar and concrete prisms in this study, only the heat cured data is reported, as no, or little expansion is observed for ambient cured concretes. In the heat cure program, the prisms were cured using a temperature program of 4 h of precure, followed by heating to 90 °C with an isotherm of 12 h prior to natural cooling to room temperature. The heating program was based on the conditions of a typical internal concrete temperature profile for precast elements with external steam curing at 55 °C, (but where no external cooling is applied) [34] where the core temperature was observed to rise to 90 °C. A precure temperature of 23 °C for the mortar prisms was used as the oven was located in a basement with a stable ambient temperature, whereas, for the concretes, a precure temperature of 30 °C was used to ensure consistent temperature for all specimens regardless of summer or winter casting as the oven used was located in a warehouse with much greater temperature variation.

Mortar shrinkage prisms (40 × 40 × 160 mm) were cast following the AS 2350.12: 2006 [40] recommended procedure. The mortar mix design is listed in Table 4. Mortar prisms, sealed in a humid atmosphere, were heat cured using a heat curing cycle of 4 h precure at 23 °C followed by heating to a measured temperature of 90 °C over a period of 2 h whereupon the temperature was held for 12 h prior to natural cooling to room temperature. At 24 h, the prisms were stripped and immersed in limewater baths and stored at 23 °C. Length measurement was carried out periodically up to 1500 days.

Table 4. Mortar Mix Design.

Material	Binder	Aggregate (Total)	Coarse Sand	Fine Sand	Water
Mix proportion by mass	1	3.0	2.5	0.5	0.45

Concrete shrinkage prisms (285 × 75 × 75 mm) were cast following the AS 1012.2, AS 1012.8.4, and AS 1012.13 recommended procedures [41]. A commercial precast concrete mix design with high cement content, low water content (0.40 w/c) and an alkali free water reducing admixture (WR), Master Builders MasterGlenium Sky 8700, was used (Table 5). The concrete prisms were heat cured using a heat curing cycle of 4 h precure at 30 °C followed by heating to 90 °C at 30 °C/hr whereupon the temperature was held for 12 h prior to natural cooling to room temperature. At 24 h, the concrete prisms were stripped and immersed in limewater baths and stored at 23 °C. Length measurement was carried out periodically for up to 800 days.

Table 5. Concrete Mix Design.

Material	Binder	Aggregate (Total)	Coarse Agg.	Fine Agg.	Water	WR	Slump
Content (kg/m^3)	450	1830	1190	640	180	1.25	120 mm
Mix proportion by mass	1	4.1	2.6	1.4	0.40	0.003	N/A

Electron microscopy was carried out using a Zeiss EVO SEM fitted with a Bruker SDD XFlash 5030 detector (Bruker, Billerica, MA, USA) for energy dispersive x-ray spectroscopy (EDS). EDS images were collected using 15 kV and 1 nA electron beam at a working distance of 13.5 mm on polished, Au-10%Pd coated specimens.

The compressive strength of concrete specimens was measured using AS 1012.9 as a guide, at a loading rate of 20 MPa/min at 1 day (2–6 h after demoulding), 28 days, 1 year and 2 years. For 1-day and 28-day strength tests, cylinder specimens were used. Specimens for 28-day tests were stored in limewater at 23 °C. For 1-year and 2-year strength tests, cubes of 75 mm were used as cut from the middle of concrete prisms with a diamond saw (Struers labotom-15 (Struers, Milton, Australia). Cube strength tests results were converted to cylinder strength by multiplying by a factor of 0.85 (EN 1992-1-2:2004 [42]).

3. Results

The expansion data for mortar is shown in Figure 1 with the SEM-EDS data shown in Figure 2. For the concrete specimens, the expansion data is shown in Figures 3 and 4 with the SEM-EDS data shown in Figure 5. 1 and 2-year expansion data for each mix are listed in Table 6. Significant expansion (>0.1% at 2 years) is only observed for mixes with elevated alkali (1% Na_2O_e) and sulphate (4% SO_3) contents (1N4$ specimens) where the expansion was observed to be >0.6%. This is consistent with the requirement for elevated alkali and sulphate content for DEF to occur coupled with heat curing. It is noted here, and is discussed further below, that the concrete OW-C 1N4$ mixes were not observed to expand. This lack of expansion is attributed to the very high C_3A content (13%) and the low $[SO_3]/[Al_2O_3]$ ratio (=0.9). For mixes where the cement composition was not spiked, the expansion has remained low (<0.12% even at 4 years (as available only for selected specimens)). For mixes where the binder contained 25% FA, expansion was less than 0.02%. More detail is provided below for each system.
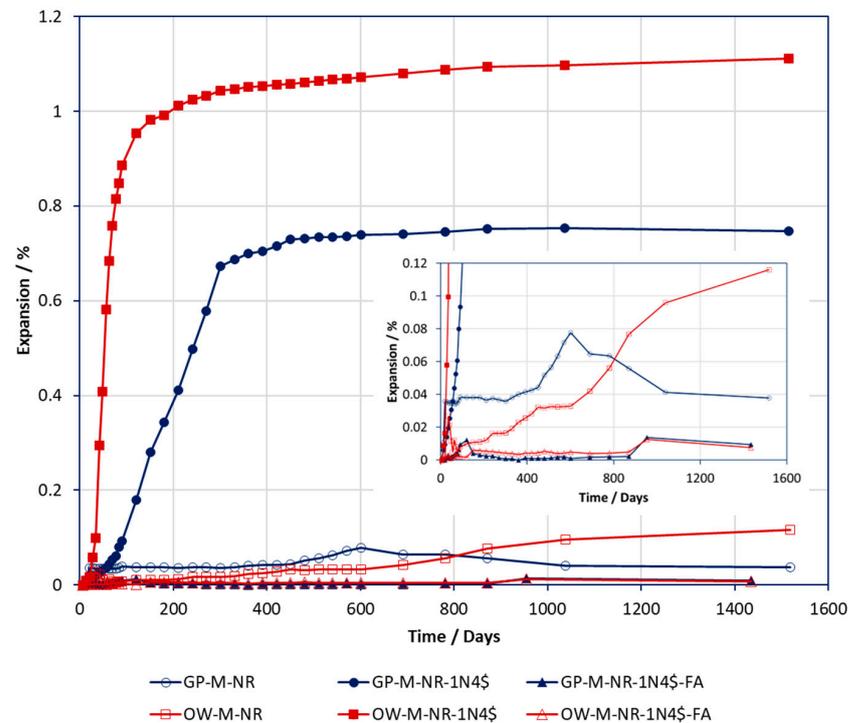
Figure 1. Expansion curves for mortar prisms (M) prepared using GP and OW cements heat cured at 90 °C for 12 h containing a non-reactive (NR) aggregate. The prisms were prepared with 'as received' cement (GP or OW) or were spiked to 1% Na_2O_e and 4% SO_3 (1N4$). Fly ash (25%) was also used as partial replacement for the cement (FA). Inset is expanded scale.

For the mortar prisms, significant expansion was observed for the 1N4$ specimens for both the GP (circa 0.7%) and the OW (circa 1.1%) cements (Figure 1). This significant expansion is related to the elevated alkali and the elevated sulphate contents present in the spiked GP and OW cements. The higher expansion for the OW mortars is consistent with the increased C_3A content for ettringite formation. For the mortar prisms which were not spiked, expansion was low, however, for the OW mortars, expansion to >0.1% at 1500 days was observed indicating that the elevated C_3A and higher SO_3 contents may result in DEF. For mortar prisms containing 25% FA, no measurable expansion was observed in the 1500 days of the trial [43].

To confirm the origin of the expansion, pieces of mortar were collected from sacrificial prisms and were mounted, polished and gold-palladium-10% coated and imaged using SEM-EDS. The resulting elemental maps are shown in Figure 2. Cracking is observed

in both expanded mortars (GP-M-NR-1N4\$ and OW-M-R-1N4\$) with the cracks filled with sulphoaluminate phases indicating ettringite. Concentrated formations of ettringite were not observed in the microstructure of any of the other specimens suggesting that the expansion observed may be attributed to DEF [31]. Additionally, unspiked prisms were not observed to expand significantly over the timeframe of the expansion tests.

For the concrete specimens prepared using a non-reactive (NR) aggregate, significant expansion was only observed for the GP-C-NR-1N4\$ prisms (Figure 3). Surprisingly, the equivalent OW-NR-1N4\$ prisms showed no significant expansion. This was attributed to the unusually high C_3A content of the OW cement at 13.1%; 4% SO_3 did not provide enough sulphate for significant DEF and resulted in a $[SO_3]/[Al_2O_3] = 0.9$ which is much less than the value of 1.1 as the required molar ratio generally reported [6]. Some expansion was observed, but it remained low (<0.04%). The conforming unspiked cement prisms showed very little expansion (<0.02%) over the 2-year period of monitoring. For this series, FA binary blends were not investigated.
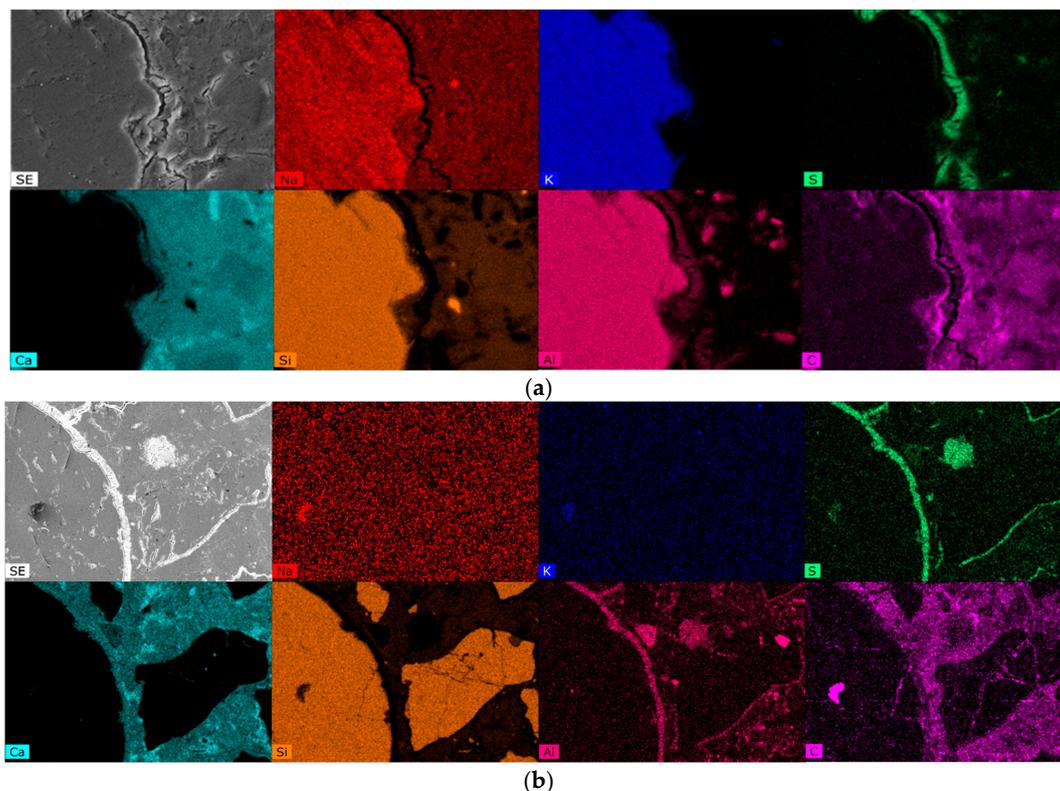
Figure 2. SEM-EDS elemental mapping at 500 days for (**a**) GP-M-NR-1N4\$ and (**b**) OW-M-NR-1N4\$ showing the secondary electron image and EDS elemental maps for Na, K, S, Ca, Si, Al and C. (Width of field is (**a**) 86 μm and (**b**) 381 μm).

For the concrete prisms prepared with a reactive aggregate (R), significant expansion was only observed for the GP-C-R-1N4\$ prisms (Figure 4). The expansion was observed to be less than that of the NR equivalent (GP-C-NR-1N4\$). Again, only minor expansion was observed for the OW equivalent (OW-C-R-1N4\$) which is consistent with the very high C_3A content reducing this concrete's susceptibility to DEF. The conforming unspiked concrete prisms showed little expansion. It is, however, notable that, although the expansion for the GP-C-R prisms was low (<0.08%) over the 2-year period of monitoring, the trend for continued increase in the expansion was observed suggesting that there is a potential for coupling of ASR and DEF [44], especially, as, in Australia, DEF is mostly observed in the presence of ASR [45,46]. For these prisms, FA binary blends were also investigated. Very low expansion (<0.01%) was observed for concrete prisms containing the 25% FA.
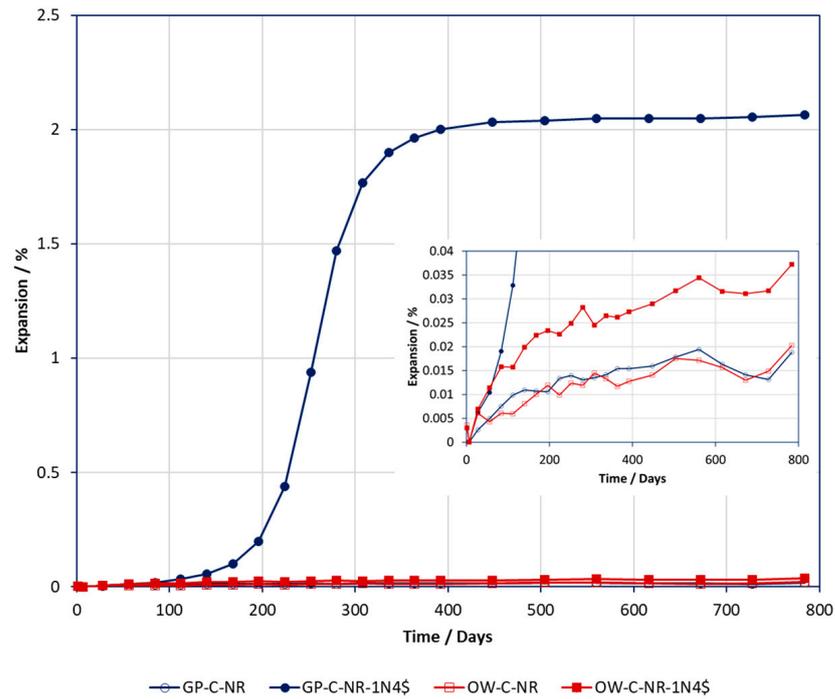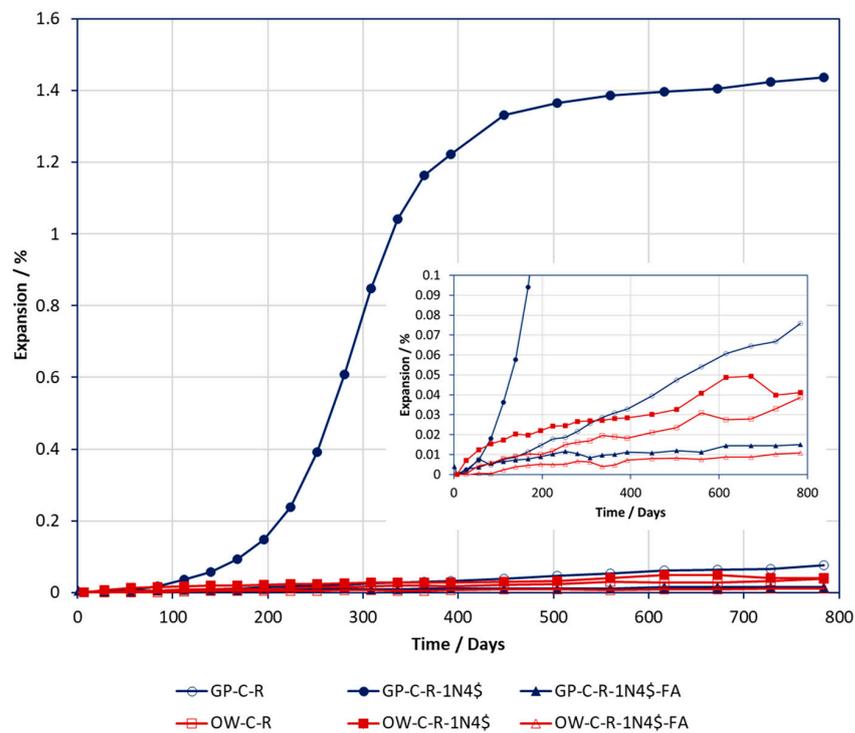
Figure 3. Expansion curves for concrete prism specimens (C) prepared using GP and OW cements heat cured at 90 °C for 12 h containing a non-reactive (NR) aggregate. The prisms were prepared with 'as received' cement (GP or OW) or the cements were spiked to 1% Na_2O_e and 4% SO_3 (1N4$). Inset is expanded scale.

Figure 4. Expansion curves for concrete prism specimens (C) prepared using GP and OW cements heat cured at 90 °C for 12 h containing a reactive (R) aggregate. The prisms were prepared with 'as received' cement (GP or OW) or the cements were spiked to 1% Na_2O_e and 4% SO_3 (1N4$). Fly ash (25%) was also used as partial replacement for the cement (FA). Inset is expanded scale.
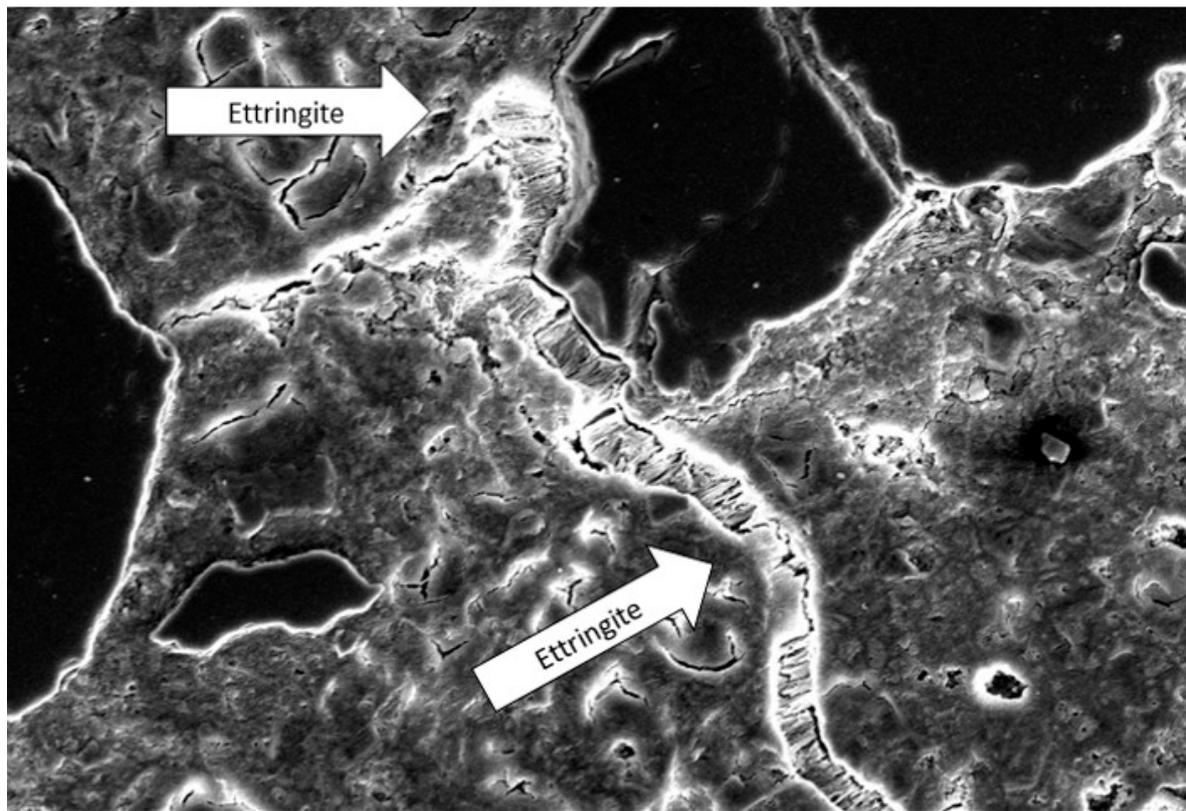
(**a**)
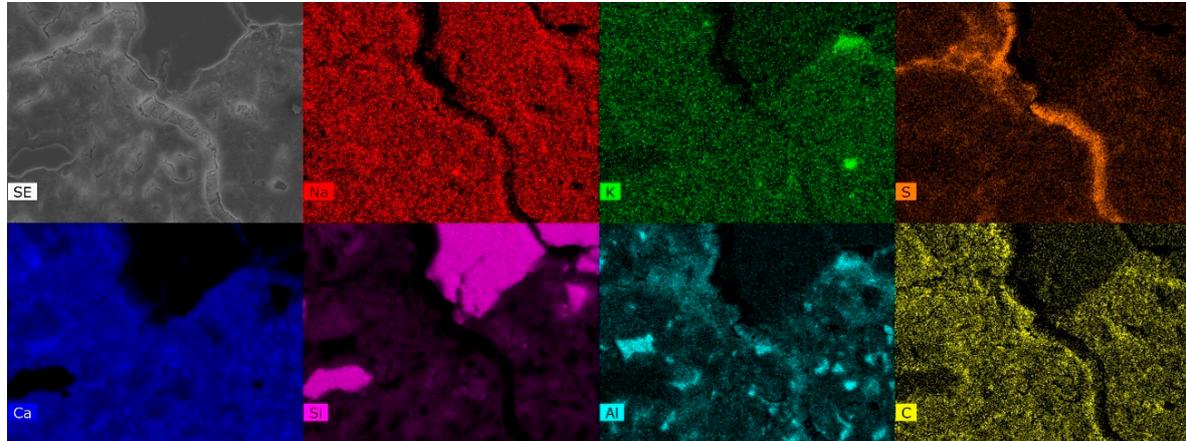
(**b**)

Figure 5. SEM-EDS elemental mapping for GP-C-NR-1N4$ at 1 year showing (**a**) the secondary electron image with ettringite crystallised in the interfacial transition zone with the crack propagating through the paste and (**b**) the secondary electron image and EDS elemental maps for Na, K, S, Ca, Si, Al and C. (Width of field is (**a**) 229 μm and (**b**) 173 μm).

SEM-EDS was carried out on polished samples of the GP-NR series of heat cured prisms. For these samples only the GP-NR-1N4$ showed evidence of microcracking. These data are shown in Figure 5. Characteristic sulphoaluminate phases were observed in the interfacial transition zone at the aggregate-cement paste interface, and migrating through the paste to indicate that DEF is responsible for the expansion. There was no evidence of ASR in the concretes made with the ASR non-reactive aggregate (NR). The presence of sulphoaluminate phases in expanded concrete coupled with the composition dependence of the expansion strongly suggest that the expansion is due to DEF.

Table 6. Expansion in % at 1 and 2 years for each of the mixes shown in Figures 1, 3 and 4.

Mix	1 Year/%	2 Year/%
GP-M-NR	0.04	0.06
GP-M-NR-1N4$	0.70	0.74
OW-M-NR	0.02	0.04
OW-M-NR-1N4$	1.05	1.08
GP-M-NR-1N4$-FA	0.00	0.00
OW-M-NR-1N4$-FA	0.00	0.00
GP-C-NR	0.02	0.01
GP-C-NR-1N4$	1.96	2.06
OW-C-NR	0.01	0.01
OW-C-NR-1N4$	0.03	0.03
GP-C-R	0.03	0.07
GP-C-R-1N4$	1.16	1.42
OW-C-R	0.02	0.03
OW-C-R-1N4$	0.03	0.04
GP-C-R-1N4$-FA	0.01	0.01
OW-C-R-1N4$-FA	0.00	0.01

The compressive strengths of the heat cured concretes made with the GP cement are shown in Figure 6. For the concretes with low alkali and sulphate contents (GP-C-NR and GP-C-R), the compressive strength continues to develop with time. The concretes made with the GP cement, but spiked to contain elevated alkali and sulphate contents (GP-C-NR-1N4$ and GP-C-R-1N4$), both show degradation of the compressive strength at 1 and 2 years corresponding with the period of expansion observed in Figures 3 and 4 [47]. The concrete containing the reactive aggregate and elevated sulphate made from the blended cement containing FA (GP-C-R-1N4$-FA) shows continued development of strength over the 2-year period. These data suggest that heat curing alone does not degrade the physical properties of the cement, however, if the alkali and sulphate contents are raised to a content which promotes DEF, degradation of the properties is observed. The use of a blended cement containing FA mitigates this degradation of the properties.
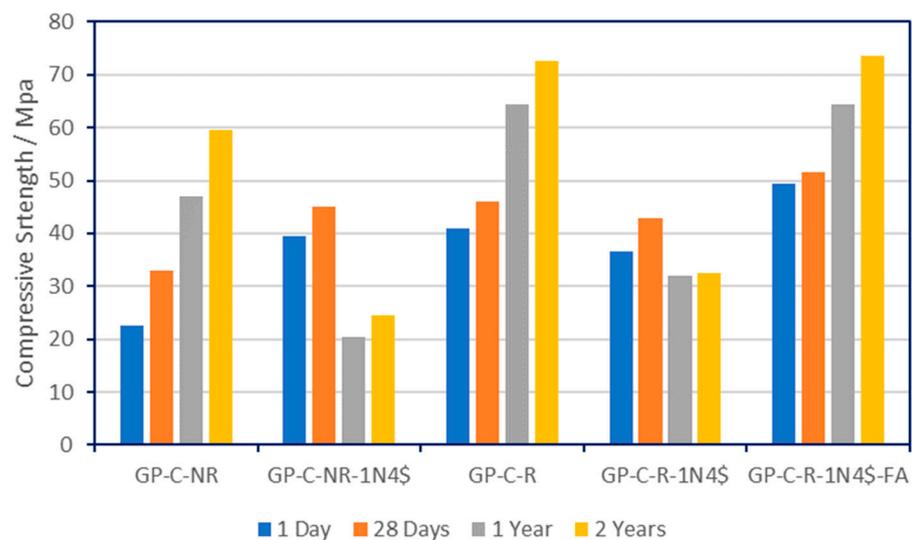

Figure 6. Compressive strength of the GP-C-NR and GP-C-R concretes for cylinders at 1 day and 28 days and for cubes at 1 year and 2 years. The compressive strength for cubes were corrected by a factor of 0.85 for comparison with the cylinder strengths.

4. Discussion

From the results presented, the risk of deleterious DEF is low for heat cured concrete manufactured using Australian standard and specified binders (AS 3972-2010 and ATIC

SP-43 [32,33]) where the alkali limit is 0.6% Na_2O_e and sulphate ion limit is 3.5% SO_3 (although a lower sulphate limit (<3% SO_3) should be considered for heat or steam cured concretes). Furthermore, concrete containing FA shows almost zero expansion even in the binder systems that have elevated alkali (1% Na_2O_e) and sulphate (4% SO_3) contents and are cured at 90 °C. The evidence suggests that heat cured concrete made with Australian commercial cements (which have low alkali and sulphate contents), with FA, are unlikely to develop deleterious DEF even if the concrete temperature exceeds the current typical limit of 70 °C or 80 °C (depending on the jurisdiction).

As the likelihood of deleterious DEF is low for binders conforming to Australian standards and specifications, the concrete mix design specifications should also be taken into account when defining specifications for heat or steam cured concretes. For concrete structures in Australia and Australian cities, the majority geographically fall into exposure classification B1 and B2 (moderate exposure classifications), according to AS 3600:2018 (Concrete Structures) or AS 5100.5:2017 (Bridge Design, Part 5: Concrete), where the use of SCMs such as FA (up to 30%) or ground granulated blast furnace slag (GGBFS; up to 40%) is suggested to prevent service life loss of the concrete [35]. Indeed, Queensland Department of Transport and Main Roads recently updated the specified temperature limit to 80 °C in order to allow for the low risk of DEF when using Australian specified cements, but requires the incorporation of SCMs as part of the binder (MRTS70 2022 [17]).

Under standard steam curing conditions when hydration is considered, the concrete temperature could increase to greater than 80 °C for large elements unless cooling strategies are implemented, or lower external temperatures are utilised. The outcome of reducing the curing temperature limit is longer curing times which reduce the productivity of precast facilities and increased cost as well as the potential for increased waste for concrete elements that are rejected as a result of transgressing specification limits.

The outcomes of the experimental program carried out in this research strongly suggests that the risk of deleterious DEF is low for concretes manufactured within compositional limits for conforming Australian cements (<0.6% Na_2O_e; <3.5% SO_3) even if the concrete temperature rises to 90 °C. Further, as FA is usually specified as part of the concrete mix design, the risk of deleterious DEF is further mitigated (even concretes susceptible to DEF through the use of non-conforming binders containing elevated sulphate and alkali contents beyond the specification limits have no observable expansion when FA is included in the mix design). Low specified temperature limits are therefore unnecessary, wasteful and reduce productivity. The specified temperature limits for concrete in precast elements should, therefore, be readdressed provided that the binder composition is tightly controlled. The specifications for the manufacture of steam or heat cured concrete elements should be based on the concrete mix design (alkali and sulphate limits of the cement and SCM use, although a lower limit for SO_3 of <3.0% is suggested as specified in TfNSW B80 for heat cured concrete rather than the 3.5% limit currently specified by AS 3972 [32] in conjunction with the maximum specified temperature), in assessing the risk of deleterious DEF rather than by generalising the curing temperature in prescriptive standard specifications.

5. Conclusions

This study has demonstrated that, for mortars and concretes where the cement conforms to the specifications outlined in AS 3972 (<3.5% SO_3) [32] and ATIC-SP43 (<0.6% Na_2O_e) [33], the risk of deleterious DEF in heat cured mortars and concretes is low. Additionally, if FA is incorporated in the binder composition, the risk is mitigated further. Specific findings are:

- For DEF to be observed, an elevated non-conforming alkali and sulphate content in the cement is required (1% Na_2O_e and 4% SO_3) in heat cured mortars and concretes at 90 °C.
- For heat cured mortars and concretes using cement (GP and OW in this study) conforming to AS 3972 (<3.5% SO_3) and ATIC-SP43 (<0.6% Na_2O_e), the risk of deleterious

DEF is low. A lower specified SO_3 limit (<3.0%) may be desirable when elevated temperature curing is carried out as specified by TfNSW B80.

- For heat cured mortars containing binary binder compositions incorporating 25% FA, no expansion was observed either when conforming or non-conforming (1.0% Na_2O_e, 4% SO_3) binders were used. For non-conforming binders where expansion was observed, the incorporation of FA in the blended cement mitigated deleterious DEF. Concretes manufactured with blended cements containing 25% FA have a very low risk of DEF even if the concrete temperature rises to 90 °C.

The results of this investigation suggest that the risk of DEF is low for concretes where the cement conforms to AS 3972 (<3.5% SO_3, although a lower specified limit of <3.0% may be preferred) and ATIC-SP43 (<0.6% Na_2O_e), and where the maximum temperature in the concrete is 90 °C. The risk of DEF is further mitigated if a binary binder composition containing 25% FA is used. The results suggest that the specification of low maximum concrete temperatures for precast concrete elements are unnecessary if the composition of the binder is tightly controlled.

References

1. Godart, B. Pathology, Assessment and Treatment of Structures Affected by Delayed Ettringite Formation. *Struct. Eng. Int.* **2017**, *27*, 362–369. [CrossRef]
2. Heinz, D.; Ludwig, U. Mechanism of secondary ettringite formation in mortars and concretes subjected to heat treatment. *Am. Concr. Inst. Spec. Publ.* **1987**, *2*, 2059–2072.
3. Ramu, Y.K. Influence of Cement Composition and Curing Regimes on the Susceptibility of Heat-Cured Cementitious Systems to Delayed Ettringite Formation. PhD Thesis, University of Technology Sydney, Ultimo, Australia, June 2020. Available online: http://hdl.handle.net/10453/142373 (accessed on 1 July 2023).
4. Taylor, H.F.W.; Famy, C.; Scrivener, K.L. Delayed ettringite formation. *Cem. Concr. Res.* **2001**, *31*, 683–693. [CrossRef]
5. Leklou, N.; Aubert, J.-E.; Escadeillas, G. Influence of various parameters on heat-induced internal sulphate attack. *Eur. J. Environ. Civ. Eng.* **2013**, *17*, 141–153. [CrossRef]
6. Zhang, Y.; Pan, Y.; Zhang, D. A literature review on delayed ettringite formation: Mechanism, affect factors and suppressing methods. *Mag. Concr. Res.* **2021**, *73*, 325–342. [CrossRef]
7. Martin, R.P.; Bonnet, A.; Renaud, J.C.; Chlela, R.; Toutlemonde, F.; Sauvaget, C. Influence of moisture on the development of delayed ettringite formation. *Mag. Concr. Res.* **2023**, *75*, 747–754. [CrossRef]
8. Paul, A.; Rashidi, M.; Kim, J.Y.; Jacobs, L.J.; Kurtis, K.E. The impact of sulfate-and sulfide-bearing sand on delayed ettringite formation. *Cem. Concr. Compos.* **2022**, *125*, 104323. [CrossRef]
9. Kawabata, Y.; Ueda, N.; Miura, T.; Multon, S. The influence of restraint on the expansion of concrete due to delayed ettringite formation. *Cem. Concr. Compos.* **2021**, *121*, 104062. [CrossRef]
10. Gu, Y.; Martin, R.P.; Metalssi, O.O.; Fen-Chong, T.; Dangla, P. Pore size analyses of cement paste exposed to external sulfate attack and delayed ettringite formation. *Cem. Concr. Res.* **2019**, *123*, 105766. [CrossRef]

11. Pichelin, A.; Carcasses, M.; Cassagnabère, F.; Multon, S.; Nahas, G. Sustainability, transfer and containment properties of concrete subject to delayed ettringite formation (DEF). *Cem. Concr. Compos.* **2020**, *113*, 103738. [CrossRef]

12. Yammine, A.; Hamdadou, M.; Leklou, N.; Bignonnet, F.; Choinska-Colombel, M. Effect of recycled concrete aggregates and recycled filler on delayed ettringite formation: An experimental study compared to chemical modelling. *Cem. Concr. Compos.* **2022**, *132*, 104636. [CrossRef]

13. Kelham, S. The effect of cement composition and fineness on expansion associated with delayed ettringite formation. *Cem. Concr. Compos.* **1996**, *18*, 171–179. [CrossRef]

14. Odler, I.; Chen, Y. Effect of cement composition on the expansion of heat-cured cement pastes. *Cem. Concr. Res.* **1995**, *25*, 853–862. [CrossRef]

15. Pourchet, S.; Regnaud, L.; Perez, J.P.; Nonat, A. Early C_3A hydration in the presence of different kinds of calcium sulphate. *Cem. Concr. Res.* **2009**, *39*, 989–996. [CrossRef]

16. Transport for NSW (TfNSW) Specification D&C B80. Concrete Work for Bridges, Edition 3, Revision 6, May 2023. Available online: https://standards.transport.nsw.gov.au/_entity/annotation/fa4dc857-cdfe-ed11-8f6d-000d3ae011f9 (accessed on 1 July 2023).

17. Transport and Main Roads Specifications MRTS70. Concrete. The State of Queensland (Department of Transport and Main Roads), July 2022. Available online: https://www.tmr.qld.gov.au/-/media/busind/techstdpubs/Specifications-and-drawings/Specifications/2-Bridges-and-Structures/MRTS70.pdf?la=en (accessed on 1 July 2023).

18. Main Roads Western Australia. Specification 820. Concrete for Structures. Clause 820.71. The Government of Western Australia, 25 July 2023. Available online: https://www.mainroads.wa.gov.au/globalassets/technical-commercial/technical-library/specifications/800-series-bridge-major-structures/specification-820-concrete-for-structures.pdf (accessed on 1 July 2023).

19. Glasser, F.P. The role of sulphate mineralogy and cure temperature in delayed ettringite formation. *Cem. Concr. Compos.* **1996**, *18*, 187–193. [CrossRef]

20. Scrivener, K.L.; Taylor, H.F.W. Delayed ettringite formation: A microstructural and microanalytical study. *Adv. Cem. Res.* **1993**, *5*, 139–146. [CrossRef]

21. Ramu, Y.K.; Thomas, P.; Sirivivatnanon, V. Pore Solution Chemistry of Expansive Heat Cured Cementitious Systems. In Proceedings of the 4th International RILEM conference on Microstructure Related Durability of Cementitious Composites (Microdurability 2020), Delft, The Netherlands, 29 April–25 May 2021; pp. 212–219. Available online: https://www.rilem.net/agenda/4th-international-rilem-conference-on-microstructure-related-durability-of-cementitious-composites-1301 (accessed on 1 July 2023).

22. Thomas, M.D.A.; Hooton, R.D.; Ramlochan, T. Use of pore solution analysis in design for concrete durability. *Adv. Cem. Res.* **2010**, *22*, 203–210.

23. Divet, L.; Randriambololona, R. Delayed ettringite formation: The effect of temperature and basicity on the interaction of sulphate and CSH phase. *Cem. Concr. Res.* **1998**, *28*, 357–363. [CrossRef]

24. Shimada, Y.; Young, J.F. Thermal stability of ettringite in alkaline solutions at 80 °C. *Cem. Concr. Res.* **2004**, *34*, 2261–2268. [CrossRef]

25. Diamond, S. Delayed Ettringite Formation–Processes and Problems. *Cem. Concr. Compos.* **1996**, *18*, 205–215. [CrossRef]

26. Miura, T.; Maruyama, I.; Nakamura, H.; Yamamoto, Y. Feedback system of ion transfer through cracks during deterioration of mortar due to sulphate attack evaluated by RBSM-truss network model. *J. Adv. Concr. Technol.* **2017**, *15*, 610–626. [CrossRef]

27. Shao, Y.; Lyansdale, C.; Lawrence, C.D.; Sharp, J.H. Deterioration of heat-cured mortars due to the combined effect of delayed ettringite formation and freeze/thaw cycles. *Cem. Concr. Compos. J.* **1997**, *27*, 1761–1771. [CrossRef]

28. Jebli, M.; Jamin, F.; Pelissou, C.; Lhopital, E.; El Youssoufi, M.S. Characterization of the expansion due to the delayed ettringite formation at the cement paste-aggregate interface. *Constr. Build. Mater.* **2021**, *289*, 122979. [CrossRef]

29. Thomas, M.; Folliard, K.; Drimalas, T.; Ramlochan, T. Diagnosing delayed ettringite formation in concrete structures. *Cem. Concr. Res.* **2008**, *38*, 841–847. [CrossRef]

30. Ramu, Y.K.; Sirivivatnanon, V.; Thomas, P.; Dhandapani, Y.; Vessalas, K. Evaluating the im-pact of curing temperature in delayed ettringite formation using electrochemical impedance spectroscopy. *Constr. Build. Mater.* **2021**, *282*, 122726. [CrossRef]

31. Ramu, Y.K.; Thomas, P.S.; Sirivivatnanon, V.; Vessalas, K. Non-expansive delayed ettringite formation in low sulphate and low alkali cement mortars. *Aust. J. Civ. Eng.* **2022**, *21*, 68–79. [CrossRef]

32. *AS 3972-2010*; General Purpose and Blended Cements. Standards Australia: Sydney, Australia, 2010.

33. Australian Technical Infrastructure Committee Specifications, ATIC-SPEC Section: SP43. Cementitious Materials for Concrete. Issue 6, 11 July 2019. Available online: http://www.atic.net.au/wp-content/uploads/2021/01/ATIC-SP43-11July2019.pdf (accessed on 1 July 2023).

34. Mak, J.; Vessalas, K.; Thomas, P.; Baweja, D. Evaluation of Factors Pertaining to Delayed Ettringite Formation in Steam Cured Precast Concrete Members. In Proceedings of the New Zealand Concrete Industry Conference 2012, Hamilton, New Zealand, 11–13 October 2012.

35. *AS 5100.5:2017*; Bridge Design, Part 5: Concrete. Standards Australia: Sydney, Australia, 2017.

36. *AS 1597.2-2013*; Precast Reinforced Concrete Box Culverts Large Culverts (Exceeding 1200 mm Span or 1200 mm Height and up to and Including 4200 mm Span and 4200 mm Height). Standards Australia: Sydney, Australia, 2013.

37. Department for Infrastructure and Transport. Master Specification ST-SC-S4 Low Pressure Steam Curing of Precast Units. The Government of South Australia, Version 2, September 2019. Available online: https://www.dit.sa.gov.au/__data/assets/pdf_file/0006/551454/MASTER_SPECIFICATION_-_PART_ST-SC-S4_-_LOW_PRESSURE_STEAM_CURING_OF_PRECAST_UNITS.DOCX.pdf (accessed on 1 July 2023).

38. VicRoads Code of Practice RC 610. Structural Concrete. 600 Series Bridgeworks. The Government of Victoria, February 2020. Available online: https://webapps.vicroads.vic.gov.au/VRNE/csdspeci.nsf/webscdocs/9D7325ADAD6BB912CA25851200151FF5?OpenDocument (accessed on 1 July 2023).

39. *AS 2758.1:2014*; Aggregates and Rock for Engineering Purposes Concrete Aggregates. Standards Australia: Sydney, Australia, 2014.

40. *AS 2350.12-2006*; Methods of Testing Portland, Blended and Masonry Cements, Method 12: Preparation of a Standard Mortar and Moulding of Specimens. Standards Australia: Sydney, Australia, 2006.

41. *AS 1012.8.4:2015*; Methods of Testing Concrete Method for Making and Curing Concrete—Drying Shrinkage Specimens Prepared in the Field or in the Laboratory. Standards Australia: Sydney, Australia, 2015.

42. *N 1992-1-2:2004*; Eurocode 2: Design of Concrete Structures—Part 1-2: General Rules—Structural Fire Design. European Committee for Standardization: Brussels, Belgium, 2004.

43. Kawabata, Y.; Takahashi, H.; Watanabe, S. The long-term suppression effects of fly ash and slag on the expansion of heat-cured mortar due to delayed ettringite formation. *Constr. Build. Mater.* **2021**, *310*, 125235. [CrossRef]

44. Yamazaki, Y.; Tsuruta, K.; Uehara, M. Effect of Alkali-silica Reaction on Delayed Ettringite Formation in Concrete. *Q. Rep. RTRI* **2020**, *61*, 192–197. [CrossRef]

45. Shayan, A.; Ivanusec, I. An experimental clarification of the association of delayed ettringite formation with alkali-aggregate reaction. *Cem. Concr. Compos.* **1996**, *18*, 161–170. [CrossRef]

46. Shayan, A.; Quick, G.W. Microscopic features of cracked and uncracked concrete railway sleepers. *Mater. J.* **1992**, *89*, 348–361.

47. Joshi, N.R.; Matsumoto, A.; Asamoto, S.; Miura, T.; Kawabata, Y. Investigation of the mechanical behaviour of concrete with severe delayed ettringite formation expansion focusing on internal damage propagation under various compressive loading patterns. *Cem. Concr. Compos.* **2022**, *128*, 104433. [CrossRef]