Durability Loss in Concrete Due to ASR-DEF, The Role of Aggregate Reactivity in Deleterious DEF

Liam Martin[1], Paul Thomas[2], Pre De Silva[3], and Vute Sirivivatnanon[2]
[1]School of Mathematical and Physical Sciences, University of Technology Sydney
[2]School of Civil and Environmental Engineering, University of Technology Sydney
[2]School of Behavioural and Health Sciences, Australian Catholic University

Abstract: Durability of concrete and cementitious materials is important to their worldwide usage in housing and infrastructure. Two known causes of durability loss in concrete are the alkali-silica reaction (ASR) and delayed ettringite formation (DEF), which are chemical processes with the potential for expansion, cracking, and strength loss in affected elements. There is significant overlap in the contributing factors for ASR and DEF, in particular pore solution alkalinity. DEF is of most concern for large, precast concrete structures, although in Australia reported cases of deleterious DEF have been in conjunction with mild or moderate ASR. Current guidelines regarding DEF are based on laboratory experiments in mortar specimens, and the role of the aggregate and ASR in concrete has been overlooked. Mitigation strategies for DEF involve temperature thresholds during curing, chemical limits for the binder, and the use of supplementary cementitious materials (SCMs) in the mix design. This study investigates the role of aggregate reactivity, curing temperature, and cement composition in the susceptibility of concrete elements to deleterious DEF, and the efficacy of fly-ash as an SCM in preventing deleterious ASR-DEF. Concrete specimens containing ASR-reactive aggregates were made with different binder and curing conditions, then monitored for expansion and strength loss over two years. Contributions towards the understanding of ASR-DEF mechanisms and the development of industry risk assessments in Australia are presented in this paper.

Keywords: durability, alkali-silica reaction, delayed ettringite formation, cement chemistry, precast concrete.

1.   Introduction

Concrete durability is an important factor in its modern use for infrastructure and buildings across the world. Concrete and other cementitious materials have many highly desirable properties for their extensive and wide range of uses in civil projects, including; in-situ placement and on-site construction, low labour and environmental costs (excluding energy and emissions of cement production), high strength, and long-term durability and efficacy. However the long service life and complex nature of composite material nature of massive concrete structures creates many potential avenues of durability loss and risk of critical failure, which can occur depending on a variety of mechanical, industry, and chemical factors [1].

Two potential causes of durability loss in concrete are the alkali-silica reaction (ASR) and delayed ettringite formation (DEF), both of which are chemical reactions that can cause expansion, microcracking, and strength loss in affected elements. ASR is a silica dissolution process between the alkaline pore solution and aggregate material containing amorphous or semi-crystalline silica (reactive aggregates), forming an expansive ASR-gel [2]. DEF is a form of internal sulfate attack with the primary mechanism being the temporary decomposition of ettringite (a sulfate mineral) during early curing, which can later reform in hardened concrete causing internal stress [3].

The non-deleterious counterpart to DEF is early ettringite formation (EEF), which is a normal part of cement hydration. From the cement binder aluminate (C_3A) and sulfate, in the form of gypsum ($C\underline{S}H_2$), react with water to form ettringite during early curing, as in Equation (1). As the concrete material is plastic at this stage, it can easily incorporate this expansive phase with no deleterious effects.

$$C_3A + 3C\overline{S}H_2 + 26H = C_3A \cdot 3C\overline{S} \cdot 32H \tag{1}$$

The mechanism of DEF is related to the solubility of sulfate in the pore solution [4]. Under conditions of elevated temperature and high alkalinity, the solubility of sulfate increases significantly leading to the dissolution of solid ettringite and/or formation of other phases, such as monosulfate. Under ambient temperate conditions or with the removal of alkali from the pore solution, sulfate solubility will drop, causing ettringite to precipitate out of solution. Thus solid ettringite and dissolved sulfate are in equilibrium in the

concrete pore solution, as in shown Equation (2). If ettringite is formed at later ages in hardened concrete, it will act as an expansive phase, creating internal stress with the potential for deleterious results.

$$ettringite \quad \overset{heat,\,alkali}{\Longleftrightarrow} \quad monosulfate + sulfate\ ions \tag{2}$$
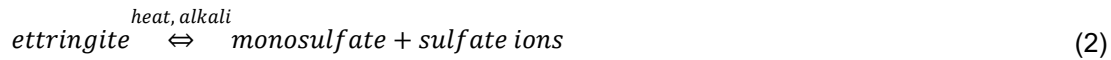
DEF is of most concern for the precast concrete industry, where early strength gain of concrete is accelerated by the application of hot steam, which has the potential to increase the risk of deleterious DEF. This is especially true for large structural elements, such as bridges, culverts, dams, and piles, where high internal heat from cement hydration can combine with external heating to cause DEF [5, 6].

In Australia, all reported cases of DEF have been in combination with mild or moderate ASR [6, 7]. This is linked to the consumption of alkali by formation of ASR gel, reducing pore solution alkalinity, increasing sulfate solubility and causing DEF. ASR-DEF can have a synergistic effect in concrete, as the progression of one reaction can accelerate the other, and resultant microcracking opening up the bulk material to further internal or external forms of chemical attack.

In order to reduce the risk of deleterious DEF for Australian concrete, industry guidelines and government standards have been developed based on laboratory tests with mortar specimens and international research [8]. For precast manufacturing temperature limits are used, with a general guide of keeping the measured temperatures to ≤ 70 – 75 °C (see QLD MRTS70, VicRoads Section 610, and NSW T HR CI 12002 ST), with recommended use of mitigation measures where the temperature exceeds these limits (eg; use of blended cements, controlled heating, etc.). For cement manufacturers, the chemical composition of the binder is tightly controlled, with low alkali and sulfate contents (see ATIC-SP 43 and AS 3972). Such specifications are conservative for risk of DEF, and can be overly restrictive or costly to industry [9]. The role of other components of concrete, specifically the aggregate and potential for ASR, have been overlooked.

The use of supplementary cementitious materials (SCMs), such as fly-ash or slag, to mitigate or prevent deleterious effects in concrete is widespread, with many local and foreign guidelines recommending it for systems at-risk of ASR, chloride ingress, and other common causes of durability loss (see HB:79). Currently some Australian specifications do call for the use of SCMs to mitigate the risk of deleterious DEF, either in the specific case as in T HR CI 12002 ST or as part of a general plan of durable design as in MRTS70. Previous research with mortar specimens has demonstrated the efficacy of fly-ash in preventing expansion associated with DEF [8, 10]. Although a common industry practice [5], the use of SCMs to reduce the risk of DEF related durability loss in concrete has not been as extensively reported in an Australian context, as compared to other concerns such as ASR or chloride attack.

1.1 *Project Outline*

Reported literature on the DEF has focused on laboratory tests with mortar specimens, with current industry guidelines for the production of cement and concrete structure design based on this research.

The impact of additional factors found in true concrete elements, including the potential for ASR, have been overlooked. This study aims to investigate the process of DEF, ASR-DEF, and potential mitigation strategies in an Australian context. The objectives of this work are to investigate the role of reactive aggregates in the susceptibility of concrete to deleterious DEF and to investigate the efficacy of SCMs, such as fly-ash, to prevent durability loss associated with DEF and ASR-DEF in concrete. A summary of findings is presented in this paper to contribute to the development of new and targeted guidelines for Australian industry groups that address ways to mitigate the risk of deleterious ASR-DEF in large concrete structures.

2. Materials & Method

Concrete specimens were manufactured for this study using locally sourced, commercially available materials complying with relevant Australian standards and industry guidelines. The binder materials used were an Australian produced general purpose (GP) cement and an Australian produced fly-ash (FA). The elemental oxide composition of these materials was determined by XRF analysis, as detailed in Table 1.

Potable tap water was used for concrete mixing and preparation of limewater tanks. An alkali-free superplasticizer (125 g/100 L) was used for sufficient workability of fresh concrete. A pessimum binder composition for deleterious DEF [8] of 1.00 % Na_2O_{eq} & 4.0 % SO_3 w/w (4.5 & 18.0 kg/m^3 respectively) was

achieved by the addition of dissolved sodium hydroxide and powdered calcium sulfate dihydrate in the correct proportions. Aggregate materials were selected according to ASR-reactivity, as classified by AS 1141.60.2. Coarse aggregates were a reactive dacite (cRe), with grading of 20 mm and 10 mm in a 3: 1 ratio. Fine aggregate was a washed, non-reactive river sand.

Table 1. Chemical composition of GP cement and fly-ash used, via XRF.

Oxide (w/w %)	L.O.I.	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	Cl	Total	Na_2O_{eq}
GP	4.0	64.1	19.4	4.9	3.0	1.2	2.6	0.17	0.45	0.037	100.1	0.47
FA	0.9	3.6	58.0	26.3	7.2	1.1	0.2	0.30	0.84	< 0.001	100.4	0.85

Concrete prisms (285 × 70 × 70 mm) and cylinders (100 × 200 mm) were manufactured according to AS 1012.2. Specimens were stored in sealed plastic bags with a humid atmosphere, then subject to curing at ambient temperature or with applied heat. The heat-curing cycle used was designed to mimic the internal temperature profile of a large precast element [5]: preset of 30 °C for 4 hrs, ramping at 30 °C/hr up to 90 °C, soak at 90 °C for 12 hrs, cool to ambient and then demould. The temperature profile of heat-cured concrete specimens is shown in Figure 1. All specimens were stored in separate limewater tanks at ambient temperature (22.9 °C ± 1.4 °C).
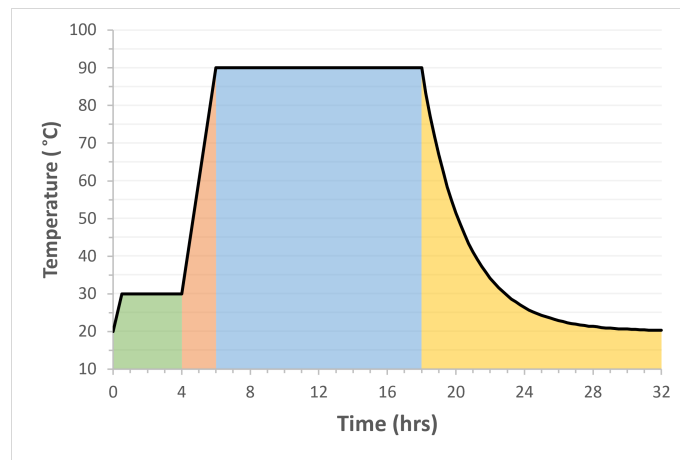

Figure 1. Temperature profile of curing regime applied to concrete specimens during early heat treatment. With stages of preset of 4 hrs at 30 °C (green), ramp to 90 °C (red), soak for 12 hrs at 90 °C (blue), followed by cooling to ambient (yellow).

The concrete mix design used was based on that of a typical large precast concrete structure, with high cement content, low water content (0.40 w/c). The slump was 120 mm, with 100 kg batch size. Details are presented in Table 2. Fly-ash was used as a replacement SCM, substituting for cement by 25 % w/w. In all other respects, the GP cement and SCM materials were considered equivalent (including binder composition and w/c ratio).

Table 2. Concrete Mix Design.

Material	Cement	Aggregate (total)	Coarse agg.	Fine agg.	Water
Content (kg/m³)	450	1830	1190	640	180

The compressive strength of concrete cylinders was measured at day 1 (after demoulding), day 28, 1 year, and at 2 years, using cylinder specimens according to AS 1012.9. The linear length of concrete prisms was

measured at day 1 (after demoulding), day 7 (as reference), day 28, every month up to 1 year, then every two months up to 2 years, using AS 1141.60.2 as a guideline. Results were averaged across 3 prisms for expansion, and 2 cylinders for strength tests.

3.   Results & Discussion

Concrete specimens were manufactured as detailed above. Binder conditions were either with cement as received ("GP, ctrl"), complying with Australian standards and specifications, cement with DEF pessimum alkali and sulfate content ("GP, 1N 4$"), or cement with pessimum and fly-ash ("GP-FA, 1N 4$"). Curing conditions were either under ambient temperature of 23 °C ("amb"), or with a heat-curing cycle ("heat"). Linear expansion and compressive strength of concrete specimens was measured over 2 years.

The limit of deleterious expansion was set at > 0.03 %, conforming with the AS 1141.60.2 test method for aggregate reactivity, with 2 years as the time limit. Note that concrete specimens were treated differently to that specified for AS 1141.60.2, with specimens immersed in limewater at 23 °C and binder contents set at 0.47 % Na_2O_{eq} & 2.6 % SO_3 (the as-received cement, "ctrl"), and 1.00 % Na_2O_{eq} & 4.0 % SO_3 (the pessimum condition for DEF, "1N 4$").

3.1   *Linear Expansion of Concrete Prisms*

Figure 2 illustrates the linear expansion of concrete systems with a pessimum binder composition, subject to curing at ambient temperature or with a heat-curing cycle. Figure 3 illustrates a magnified view of the linear expansion of concrete systems with a range of binder conditions, subject to ambient or heat-curing. Full results are summarised in Table 3.

For concrete systems with binder pessimum of 1.00 % Na_2O_{eq} and 4.0 % SO_3 (and no replacement fly-ash), significant deleterious expansion was observed in heat-cured specimens and minor deleterious expansion found in ambient-cured specimens, with final expansion at 2 years of 1.58 % and 0.06 % respectively.
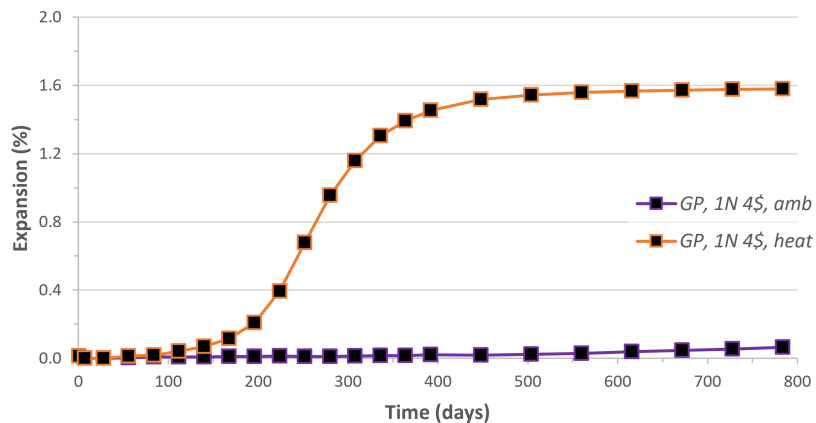

Figure 2. Linear expansion of concrete specimens with pessimum binder, and subject to ambient or heat-curing.

The expansion for heat-cured specimens was attributed to ASR-DEF, with DEF as the primary cause. This was confirmed via electron microscopy of selected samples, which found ASR gel and localised ettringite phases along the aggregate-paste boundary. The conditions of high alkali content of the mix and high and sustained temperatures during early curing acted as processing factors in the DEF mechanism, temporarily increasing the solubility of sulfate in the pore solution and preventing normal EEF during cement hydration. The conditions of high sulfate content of the binder, and with normal aluminate content, acted as reactant factors in the DEF mechanism, increasing the amount of sulfate phases that can be formed in the concrete, including ettringite.

The observed expansion followed a S-shape curve, which is classic behaviour of DEF [3, 8], with large and early expansion of 0.08 % at 150 day, exponential growth up to an inflection point at 250 days, then slowing to a final plateau of 1.5 – 1.6 % at 450 days and beyond. The magnitude of expansion was large compared to the deleterious limit of 0.03 % (which is based on ASR test methods), but comparable to prior research results with mortar specimens of 0.2 – 0.5 % expansion [3, 6].
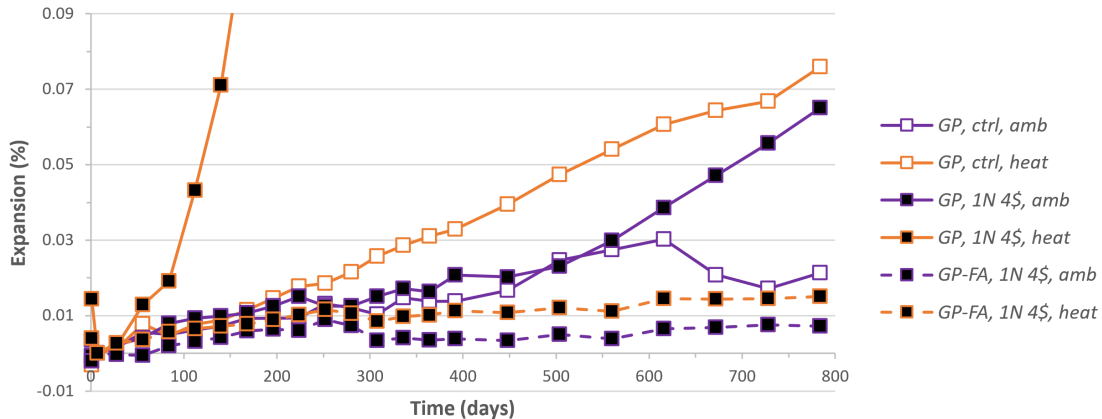

Figure 3. Linear expansion of concrete specimens, subject to different binder and curing conditions.

The expansion for specimens cured at ambient temperature was attributed to ASR, with characteristic slow but steady expansion [2], which was confirmed by electron microscopy by the presence of ASR gel. The conditions of an elevated alkali mix content and presence of reactive aggregate material led to the formation and expansive swelling of ASR gel, following ASR reaction mechanisms. In relation to AS 1141.60.2, the Concrete Prism Test (CPT) method, deleterious expansion attributed to ASR was observed in specimens. This is despite the lack of accelerated test conditions as compared between CPT and experiment methods, namely that of temperature (38 °C vs. 23 °C) and alkali content (1.25 % vs. 1.00 % Na_2O_{eq} of binder, or 5.2 kg/m^3 vs. 4.5 kg/m^3 by total weight).

For concrete systems with cement as received, minor deleterious expansion was observed in heat-cured specimens at later ages and no deleterious expansion was found in ambient-cured specimens, with final expansion at 2 years of 0.07 % and 0.02 % respectively. The expansion in heat-cured specimens was attributed to DEF, which was confirmed by electron microscopy with the presence of ettringite. Although ASR gel was not found in the control heat-cured specimens, it is likely that the observed expansion is due to a combination of DEF induced by heat-curing and the progression of ASR depleting alkali concentration in the pore water, which reduces the aqueous solubility of sulfate and promotes the further formation of ettringite.

For concrete systems with pessimum binder composition and fly-ash as a replacement SCM (25 % w/w), no deleterious expansion was observed in either ambient or heat-cured specimens, with final expansion at 2 years of > 0.02 % for both systems. The fact that no expansion was found even in systems considered at risk of ASR or ASR-DEF, as in comparable systems without fly-ash, is evidence that fly-ash as an SCM acts to prevent deleterious reactions occurring in concrete. This is well-known for ASR, with extensive history, usage, and continuing investigation [2]. However for DEF, there has been limited research in the practice to address specific risks and concerns associated with deleterious DEF.

How fly-ash acts to mitigate or prevent deleterious DEF and/or ASR-DEF is the subject of ongoing research. Two proposed mechanisms are via pore-blocking or acting as a reactive agent. Pore-blocking of the cement paste material would prevent reactive species such as alkali and sulfate from moving between chemical reservoirs and reaction sites, thus stopping ettringite formation. As a reactive material, the formation of C-S-H or C-A-S-H gels could serve to adsorb sulfate ions and disperse ettringite formation away from the aggregate-paste boundary, reducing the total magnitude of internal stress in the bulk material. Alternatively, aluminate released into the pore solution could inhibit the DEF reaction. The study of these and other pathways is the subject of ongoing research by the authors.

Table 3. Linear expansion of concrete specimens (%).

Day	Concrete systems					
	GP, ctrl, amb	GP, ctrl, heat	GP, 1N 4$, amb	GP, 1N 4$, heat	GP-FA, 1N 4$, amb	GP-FA, 1N 4$, heat
1	0.004	-0.003	-0.001	0.014	-0.002	0.004
7*	0.000	0.000	0.000	0.000	0.000	0.000
28	0.002	0.001	0.002	0.002	0.000	0.003
56	0.006	0.008	0.004	0.013	-0.001	0.004
84	0.005	0.005	0.008	0.019	0.002	0.006
112	0.006	0.008	0.009	0.043	0.003	0.006
140	0.007	0.009	0.010	0.071	0.004	0.007
168	0.009	0.011	0.011	0.116	0.006	0.008
196	0.009	0.015	0.013	0.208	0.006	0.009
224	0.009	0.018	0.015	0.393	0.006	0.010
252	0.013	0.019	0.013	0.679	0.009	0.012
280	0.012	0.022	0.013	0.955	0.007	0.011
308	0.010	0.026	0.015	1.157	0.003	0.008
336	0.015	0.029	0.017	1.304	0.004	0.010
364	0.014	0.031	0.016	1.392	0.004	0.010
392	0.014	0.033	0.021	1.453	0.004	0.011
448	0.017	0.040	0.020	1.516	0.003	0.011
504	0.025	0.047	0.023	1.544	0.005	0.012
560	0.027	0.054	0.030	1.557	0.004	0.011
616	0.030	0.061	0.039	1.566	0.006	0.014
672	0.021	0.064	0.047	1.571	0.007	0.014
728	0.017	0.067	0.056	1.577	0.007	0.015

*Reference measurement for calculation of total length change.

3.2 Compressive strength of Concrete

Figure 4 illustrates the compressive strength of concrete systems with binder conditions of cement as received, with pessimum composition, or with pessimum and fly-ash, subject to curing at ambient temperature or with a heat-curing cycle. Results are summarised in Table 4. Note that for all concrete systems, measured strength as compared between curing conditions was higher for heat-curing than for ambient at day 1, while the reverse was true for day 28. This is normal behaviour for heat-treated or precast concrete, which uses accelerated curing conditions to sacrifice late strength gain for early age strength [5].
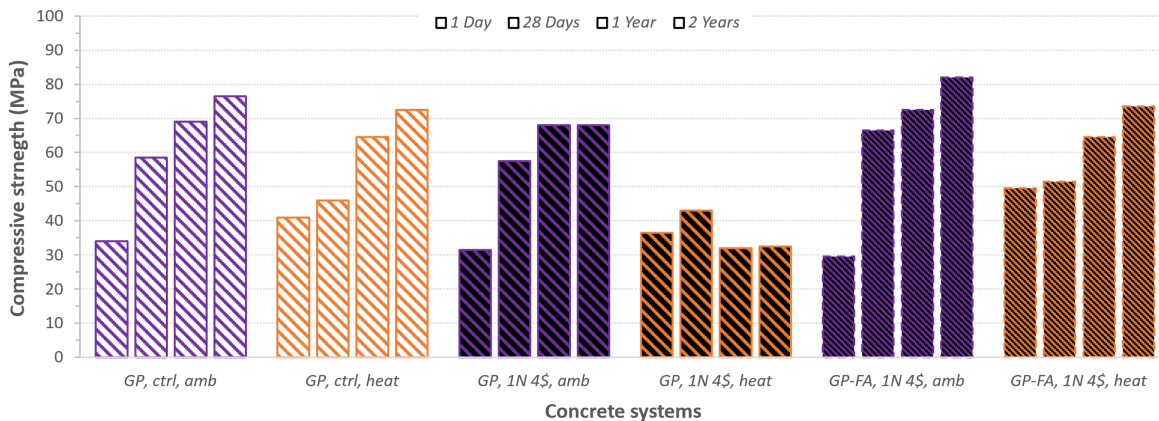

Figure 4. Compressive strength of concrete specimens subject to different binder and curing conditions. Individual results displayed left-to-right; 1 day, 28 days, 2 years.

For concrete systems with pessimum binder composition and no fly-ash, severe strength loss was observed in heat-cured specimens and minor strength loss was observed in ambient-cured specimens. This strength loss followed the progression of deleterious expansion, and was attributed to ASR-DEF in the case of specimens with heat-curing and to ASR for specimens with no heat-curing.

For concrete systems with cement as received, no strength loss was observed in either ambient or heat-cured specimens. This is contrast to the expansion results for the heat-cured specimens, which did show deleterious expansion associated with DEF at the 2-years of age. Thus signs of expansion above the 0.03 % limit should not be taken as indicative of or confirmation of durability loss due to ASR-DEF in concrete, with special consideration when extrapolating laboratory results to comparable real-world structures.

For concrete systems with pessimum and fly-ash, no strength loss was observed in either ambient or heat-cured specimens. As in the case of linear expansion results, this is despite the corresponding systems with no fly-ash experiencing severe deleterious effects associated with ASR-DEF. This is further evidence of the efficacy of fly-ash as an SCM in preventing durability loss from ASR-DEF.

Table 4. Compressive strength of concrete specimens (MPa).

System	1 Day	28 Days	1 Year	2 Years
GP, ctrl, amb	34.0	58.5	69.0	76.5
GP, ctrl, heat	41.0	46.0	64.5	72.5
GP, 1N 4$, amb	31.5	57.5	68.0	68.0
GP, 1N 4$, heat	36.5	43.0	32.0	32.5
GP-FA, 1N 4$, amb	29.5	66.5	72.5	82.0
GP-FA, 1N 4$, heat	49.5	51.5	64.5	73.5

4.   Conclusions

This research investigated the role of the alkali-silica reaction in the susceptibility of concrete to delayed ettringite formation, and the efficacy of fly-ash as an SCM to mitigate durability loss in concrete associated with ASR-DEF, via concrete specimens as measured over two years. Concrete specimens similar to large precast elements were manufactured, using ASR-reactive aggregates, with or without a heat-curing cycle, and a range of binder conditions.

Significant deleterious expansion and severe strength loss was found in heat-cured concrete specimens with elevated alkali and elevated sulfate contents, which was attributed to ASR-DEF. Minor deleterious expansion and strength loss was found in corresponding specimens cured at ambient temperature, which was attributed to ASR. For corresponding cement systems using fly-ash as an SCM, no deleterious expansion or strength loss was observed in specimens for either curing conditions, with normal performance. This is evidence that fly-ash is a suitable mitigation strategy to prevent durability loss associated with ASR-DEF in at-risk concrete structures. Minor deleterious expansion was found in heat-cured concrete specimens and locally produced Australian cement. No associated strength loss was observed. This was attributed to DEF with potential contribution of ASR.

Based on observed behaviour with concrete specimens, current industry guidelines and specifications concerning the manufacture of large precast elements carry a low risk of deleterious ASR-DEF. Structures utilising a binder with elevated alkali and sulfate contents or with ASR-reactive aggregates, which have a high risk of ASR-DEF, should strongly consider the use of SCMs such as fly-ash to mitigate potential durability loss associated with ASR-DEF. Future changes to existing guidelines or standards for risk of DEF in Australia should incorporate this recommendation.

5.   Acknowledgement

6.   References

1.   Hooton, R.D. and J.A. Bickley, *Design for durability: The key to improving concrete sustainability.* Construction and Building Materials, 2014. **67**: p. 422-430.
2.   Rajabipour, F., et al., *Alkali–silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps.* Cement and Concrete Research, 2015. **76**: p. 130-146.
3.   Taylor, H.F.W., C. Famy, and K.L. Scrivener, *Delayed ettringite formation.* Cement and Concrete Research, 2001. **31**(5): p. 683-693.
4.   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.
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.
6.   Shayan, A. and G.W. Quick, *Microscopic Features of Cracked and Uncracked Concrete Railway Sleepers.* ACI Materials Journal, 1992. **89**(4).
7.   Au, J. and A. Peek. *A case study review of concrete deterioration by ASR/DEF.* in *18th International Corrosion Congress 2011.* 2011.
8.   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.
9.   Melchers, R.E., et al., *Long-term durability of reinforced concrete piles from the Hornibrook Highway Bridge.* Australian Journal of Structural Engineering, 2017. **18**(1): p. 41-57.
10.   Shayan, A., R. Diggins, and I. Ivanusec, *Effectiveness of fly ash in preventing deleterious expansion due to alkali-aggregate reaction in normal and steam-cured concrete.* Cement and Concrete Research, 1996. **26**(1): p. 153-164.