

Role of Aggregate Reactivity, Binder Composition, and Curing Temperature on the Delayed Ettringite Formation and Associated Durability Loss in Concrete



L. Martin, P. Thomas, P. De Silva, and V. Sirivivatnanon

Abstract The durability of concrete is critical to its worldwide use as a structural material for buildings and infrastructure, with the lifetime service of concrete greatly affecting its economic, environmental, and social costs. Causes of durability loss in some concrete structures can be attributed to the alkali–silica reaction (ASR) and delayed ettringite formation (DEF). Both are chemical reactions that have the potential to cause expansion and strength loss in affected elements. Significant overlap exists in the factors contributing to ASR and DEF in concrete structures, with widely reported evidence of deleterious DEF frequently occurring in conjunction with mild or moderate ASR. For precast concrete, experiments in mortars have provided limits in the alkali and sulfate content of the binder and maximum curing temperatures used to minimize DEF risk. The role of other constituents in concrete specimens, notably the aggregate, has been overlooked. We investigated the role of reactive aggregates and ASR in the susceptibility of concrete to deleterious DEF.

Keywords Alkali-silica reaction · Delayed ettringite formation · Durability loss · Heat cure · Precast concrete

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1 Introduction

The durability of concrete as a structural material is vitally important to its modern use in buildings, homes, and infrastructure around the world. Concrete and cement-based materials have many desirable properties for use in a variety of structures, allowing in-form construction, low labor cost, low technical threshold, low cost and environmental concerns (excluding high carbon emissions), high strength, good durability, and long-term efficacy [1, 2]. However, the extended service life, multi-faceted application, and complex nature of concrete as a composite material creates many potential causes of durability loss across the structural, mechanical, and chemical fields. These include acid, chloride, or sulfate attack, steel corrosion, leeching, freeze–thaw events, salt and de-icing ingress, humidity cycles, and erosion [3, 4].

Two potential causes of durability loss in concrete structures are the alkali–silica reaction (ASR) and delayed ettringite formation (DEF), both of which are chemical reactions that can lead to deleterious expansion, microcracking, and strength loss in affected elements. DEF is a form of internal sulfate attack in concrete, with the primary mechanism being the dissolution–precipitation reaction of the sulfate mineral ettringite, which can cause expansion and cracking [5]. DEF is of most concern in the precast concrete industry, where the conditions used to accelerate the strength gain of concrete have the potential to increase the risk of deleterious DEF [6]. The ASR is a chemical reaction in concrete involving the alkaline pore solution and aggregate material containing non-crystalline silica, leading to the formation of an expansive ASR–gel phase and the potential for expansion and cracking [7]. In many real-world instances of DEF, ASR was also found in [8–10]. In an Australian context, all reported cases of DEF in concrete have been in conjunction with mild or moderate ASR, and have been linked to cracking in steam-cured precast concrete and massive concrete elements [6]. Thus, manufacturing specifications for precast and/or large concrete have a conservative view to DEF risk, leading to restrictive processing methods and substantial industry costs [6, 11].

The DEF mechanism is based on the solubility of sulfate in the pore solution of concrete. Ettringite normally forms during early cement hydration, with no negative effects on the final concrete material. Elevated temperatures and alkalinity (high pH) result in the decomposition of ettringite, and when the concrete system returns to normal conditions of temperature and alkalinity, ettringite will recrystallize [12]. The slow precipitation of ettringite as an expansive phase in hardened concrete at later ages induces cracking and strength loss. To minimize the risk of deleterious DEF, temperature limits are used in the manufacturing of precast concrete, as based on laboratory mortar tests and chemical composition of the cement [6, 13]. The role of other components of concrete, specifically the aggregate, has been downplayed.

1.1 Project Outline

Available literature and research results concerning DEF have focused on laboratory experiments in mortars with modified cement systems. Guidelines and specifications for cement production and the design of concrete structures are based on these findings by convention. The consideration of additional factors found in true concrete elements, including the potential for ASR, has been overlooked. Evidence-based contributions to this topic will assist in the development of targeted guidelines and standards for the precast concrete industry and mitigation of DEF risk in modern structures. By increasing the confidence in the best use of construction materials, our research will help reduce the environmental, economic, and social costs of steam-cured concrete elements and the risk of catastrophic failure.

The aim of this research work was to investigate the process of DEF and the role of aggregate reactivity, binder composition, and curing temperature on the susceptibility of concrete systems to deleterious DEF and ASR–DEF. The primary objectives of this study were to identify the conditions in concrete containing nonreactive aggregates that can induce deleterious DEF, specifically related to cement composition and curing conditions, and to investigate the role of reactive aggregates on the susceptibility of concrete to deleterious DEF.

2 Methods

The manufacture of concrete specimens for this study was carried out using local sourced materials, complying with relevant Australian standards and industry guidelines. The binder used was an Australian produced, commercial grade general-purpose (GP) cement. The elemental oxide composition of the cement was determined by X-ray fluorescence (XRF) analysis, with results presented in Table 1.

Potable tap water was used for mixing of concrete and preparation of saturated limewater. To retain sufficient workability of freshly mixed concrete, an alkali-free superplasticizer was used (125 g/100 L).

Previous literature has reported a pessimum (worst case) condition for binder compositions of alkali and sulfate content with regards to deleterious DEF [13, 14]. For pessimum concrete specimens, the alkali and sulfate binder content was increased to 1% $\text{Na}_2\text{O}_{\text{eq}}$ (4.5 kg/m^3) and 4% SO_3 (18.0 kg/m^3) by the addition of dissolved sodium hydroxide and powdered calcium sulfate dihydrate respectively. Aggregate materials used were selected according to ASR-reactivity, as classified by Australian

Table 1 Chemical composition of GP cement via XRF

Component	L.O.I	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O	K ₂ O	Cl	Total	Na ₂ O _{eq}
Content (w/w %)	4.0	64.1	19.4	4.9	3.0	1.2	2.6	0.17	0.45	0.037	100.1	0.47

Table 2 Concrete mix design

Property	Cement content	Coarse aggregate	Fine aggregate	w/c ratio	Batch size	Slump
Detail	450 kg/m ³	1190 kg/m ³	640 kg/m ³	0.40	100 kg	120 mm

standards AS1141.60.2 for coarse aggregates and AS1141.60.1 for fine aggregates. Coarse material was either a nonreactive basalt (nRe) or reactive dacite (cRe), with a grading of 20 and 10 mm in a 3:1 ratio. The fine material was a washed nonreactive river sand. Concrete prisms (285 × 70 × 70 mm) were manufactured using AS1012.2 as the guide for preparation and mixing, and AS1141.60.2 for the design of prisms, with three prisms for each set of results. Concrete cylinders (100 × 200 mm) were also manufactured, with two cylinders for each set. The concrete mix design, presented in Table 2, was based on a typical large structural element manufactured by the Australian precast industry, utilizing a high cement content and low water content.

Concrete specimens were cured under one of two conditions: curing at ambient temperature (23 ± 2 °C) or heat-cured. The heat-curing process was designed to follow the internal temperature profile of a large precast element [11]; preset of 30 °C for 4 h, heating of 30 °C/h up to 90 °C, soak at 90 °C for 12 h, then cooling to ambient temperature and demolding. During curing, all specimens were stored in sealed plastic bags, with a damp cloth as the moisture source. After demolding, specimens were stored in limewater tanks at ambient temperature. The compressive strength of the concrete specimens was measured at 1 day and 28 days with cylinders, and at 1 year with cubes cut from the prisms (75 mm, 2 cubes), as per AS1012.9. Concrete prisms were measured for linear length and mass, using AS1141.60.2 as the guide, at day 1, day 7 as reference, day 28 and then at monthly intervals up to 1 year.

3 Results and Discussion

Concrete specimens were manufactured as detailed above, with varying binder (pessimum/1N 4\$ or control/ctrl), aggregate (reactive/cRe or nonreactive/nRe), and curing (ambient/amb or heat-cured/heat) conditions linked to the occurrence of ASR, DEF, and ASR–DEF. Linear expansion and mass of prisms was monitored over 1 year, and compressive strength was measured at 1 day, 28 days, and 1 year.

“DEF-only” systems had only nRe aggregates present and thus minimal potential for ASR; “ASR–DEF” systems had cRe aggregates present and thus ASR could occur; “pessimum” systems had an altered binder of 1.00% Na₂O_{eq} and 4.0% SO₃, which increased the risk of DEF; “Control” systems used the binder as received, complying with the standards and chemical content limits of Australia.

The threshold for deleterious expansion was arbitrarily set at 0.03% of total linear length, based on the Australian aggregate reactivity test method AS1141.60.2. Note

that the specimens were treated differently in this study compared with AS1141.60.2, specifically being immersed in limewater tanks at normal temperature (23 °C) and lower alkali binder content (1% Na₂O_{eq}).

3.1 DEF in Concrete

Concrete specimens were manufactured with selected binder and curing conditions to promote deleterious DEF in the absence of potential ASR. Linear expansion, mass gain, and compressive strength were measured over 1 year, as shown in Fig. 1.

Deleterious expansion and strength loss were observed only in specimens subject to pessimum binder content and sustained heat-curing, and they were attributed to DEF. All other concrete systems, with either curing at ambient temperature or as-received cement, did not show deleterious effects or durability loss. This supports the

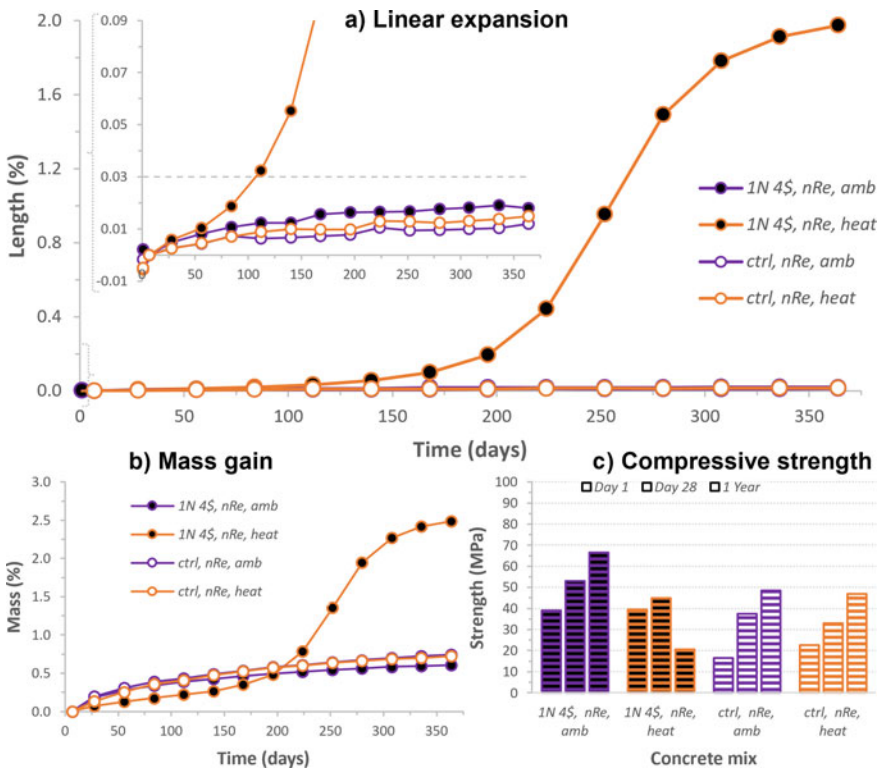


Fig. 1 Physical characteristics of concrete prisms with nonreactive (nRe) aggregates, showing **a** linear expansion; **b** mass gain and **c** compressive strength, over 1 year. Binder used was at pessimum condition (1% alkali, 4% sulfate/1N 4\$) or as received (control/ctrl), curing was at ambient temperature (23 °C/amb) or heat-cured (90 °C for 12 h/heat)

current understanding that high temperature, elevated alkali, and elevated sulfate are all essential factors for the occurrence of deleterious DEF in concrete. For structures without any of these factors present, the risk of durability loss due to DEF is predicted to be minimal.

Observed expansion in the heat-cured pessimum prisms was significant, reaching 2% total of original length at 1 year, with expansion slowed but ongoing in the final months of measurement. It is expected that ongoing change would plateau in a further 6 months. This overall expansion was severe but comparable to other reported results of deleterious DEF, ranging from 1.2 to 1.8% [13]. For all other systems, the expansion was below the 0.03% threshold at 1 year, with decreasing expansion of pessimum/ambient, control/heat-cured, and control/ambient as the least. These minor variations were attributed to increased porosity of heat-cured cement paste [6, 14], and the sulfate addition inducing limited early expansion [4].

Changes in the mass of the concrete specimens closely followed that of expansion, with only the pessimum/heat-cured system showing a large expansion of 2.5% at 1 year. All other concrete systems only had minor increases to the total mass after 1 year. This large change was attributed to two causes: the inflection of the expansion curve indicating rapid development of new phases, including ettringite, which retains significant amounts of water in bound hydrates, and the formation of microcracks across the bulk material from internal expansive stress leading to ingress and uptake of water.

Similarly with the strength of the concrete specimens, significant strength loss was observed only in pessimum/heat-cured systems and attributed to DEF, with measured strength at day 28 to 1 year decreasing from 45 MPa to 20.5 MPa, respectively. Again, all other concrete systems showed strength gain as expected. For day-1 strength, heat-cured specimens were equivalent to or better than the corresponding ambient-cured specimens, as expected with precast manufacturing of concrete [15]

3.2 ASR-DEF in Concrete

Concrete specimens containing cRe aggregates were manufactured with selected binder and curing conditions to promote deleterious DEF, with the potential of ASR. Linear expansion, mass gain, and compressive strength were measured over 1 year, shown in Fig. 2.

Measured linear expansion, mass gain, and compressive strength of the ASR-DEF systems followed the same pattern as that of the DEF-only systems, with concrete systems with pessimum conditions and heat-curing exhibiting deleterious results over 1 year, while all other systems did not. For the pessimum/heat system, observed results at 1 year were expansion of 1.4%, mass gain of 2.0%, and compressive strength of 43.0 MPa at 28 days to 32.0 MPa at 1 year. The exception to this was minor expansion in the control/heat-cured system, reaching 0.03% at 1 year, with no corresponding change in mass or strength. This was attributed to increased porosity and alkali release of the cement paste due to the heat-curing process, leading to ASR.

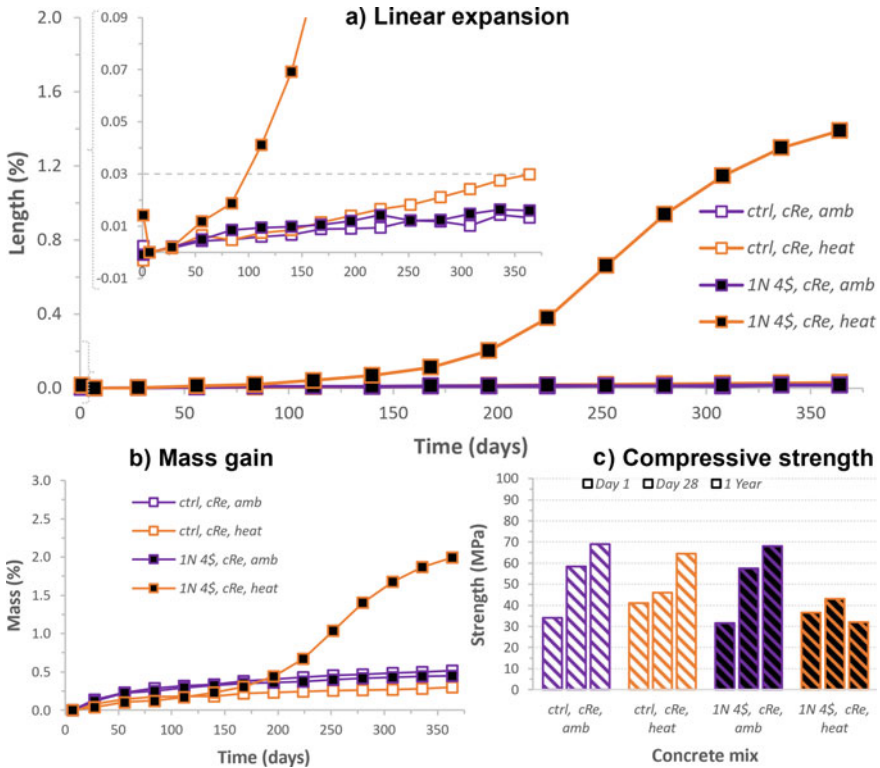


Fig. 2 Physical characteristics of concrete prisms with coarse reactive (cRe) aggregates, showing **a** linear expansion; **b** mass gain; and **c** compressive strength, over 1 year. Binder used was at pessimum condition (1% alkali, 4% sulfate/1N 4\$) or as received (control/ctrl), curing was at ambient temperature (23 °C/amb) or heat-cured (12 h at 90 °C/heat)

Comparing the deleterious DEF-only and ASR–DEF systems, the most significant difference was the reduced magnitude of durability loss in the concrete specimens. The pessimum/heat-cured DEF-only system had more expansion, mass gain, and strength loss than the equivalent system with cRe aggregates present at 1 year. One possible cause is the development of ASR and related phases slowing the DEF process and reducing the total amount of microcracking and expansive phases. In this scenario, reactive silica and small amounts of ASR–gel could act as a weak supplementary cementitious material (SCM), blocking transport pores, dispersing ettringite away from the aggregate–paste boundary, and creating micro-voids for ettringite to form in without restraint. Supporting evidence can be found in the efficacy of SCMs such as fly ash to mitigate DEF [11], and the use of finely ground reactive aggregates as replacement SCMs [16]. Otherwise, the trajectory of change in expansion remained the same, with high early expansion (75–150 days), divergence (200 days), and reduced rate in the later months (300–350 days).

4 Conclusions

This research investigated the role of the ASR in the susceptibility of concrete to DEF via an experimental study with concrete specimens. The factors of alkali, sulfate, temperature, and aggregate reactivity were assessed for their contribution to deleterious DEF and ASR–DEF in concrete.

Deleterious DEF was not observed in concrete specimens prepared with locally produced Australian cement, which is linked to the low alkali and low sulfate binder content. Binder systems with elevated alkali and sulfate content increase the risk of deleterious DEF. The combination of binder composition with high alkali (1.00% $\text{Na}_2\text{O}_{\text{eq}}$) and high sulfate ($\text{SO}_3\%$) content, and curing conditions of high temperature (90 °C) and sustained heat (12 h) are necessary for deleterious DEF to occur in concrete. Specimens not subjected to these conditions did not exhibit deleterious expansion during 1 year of measurement.

Reactivity of aggregates influences expansion attributed to DEF, but only in the presence of pessimum conditions and heat-curing. Observed durability loss with expansion, mass gain, and strength loss was greater in DEF-only systems compared with ASR–DEF systems.

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