Available online at www.sciencedirect.com

ScienceDirect

Cement and Concrete Research 38 (2008) 841 – 847

Cement and Concrete Research

Diagnosing delayed ettringite formation in concrete structures

Michael Thomas [a,*], Kevin Folliard [b], Thano Drimalas [b], Terry Ramlochan [c]

[a] *University of New Brunswick, United States*
[b] *University of Texas at Austin, United States*
[c] *University of Toronto, Canada*

Received 7 October 2007; accepted 8 January 2008

Abstract

There has been a number of cases involving deteriorated concrete structures in North America where there has been considerable controversy surrounding the respective contributions of alkali–silica reaction (ASR) and delayed ettringite formation (DEF) to the observed damage. The problem arises because the macroscopic symptoms of distress are not unequivocal and microscopical examinations of field samples often reveal evidence of both processes making it difficult to separate the individual contributions. This paper presents the results of an investigation of a number of concrete columns carrying a raised expressway in North America; prior studies had implicated both DEF and ASR as possible causes of deterioration. Although the columns were not deliberately heat-cured, it is estimated that the peak internal temperature would have exceeded 70 °C and perhaps even 80 °C, in some cases. The forensic investigation included scanning electron microscopy with energy-dispersive X-ray analysis and expansion testing of cores extracted from the structure. Small-diameter cores stored in limewater expanded significantly (0.3 to 1.3%) and on the basis of supplementary tests on laboratory-produced concrete specimens it was concluded that expansion under such conditions is caused by DEF as the conditions of the test will not sustain ASR. In at least one column, DEF was diagnosed as the sole contributory cause of damage with no evidence of any contribution from ASR or any other deterioration process. In other cases, both ASR and DEF were observed to have contributed to the apparent damage. Of the columns examined, only concrete containing fly ash appeared to be undamaged. The results of this study confirm that, under certain conditions, the process of DEF (acting in isolation of other processes) can result in significant deterioration of cast-in-place reinforced concrete structures.

Keywords: Alkali–silica reaction (ASR); Delayed ettringite formation (DEF); Scanning electron microscopy (SEM)

1. Introduction

In a previous paper [1] presented the results of a forensic evaluation conducted on core samples retreived from precast, prestressed concrete bridge girders. These girders were exhibiting extensive cracking, which was fortunately observed before the girders were placed in service, and were then subjected to examination by numerous investigators. It was generally agreed by all who examined samples from these girders that the concrete was undergoing some form of internal chemical attack, however, there was considerable debate as to whether the principal cause of deterioration was alkali–silica reaction (ASR) or delayed ettringite formation (DEF). Scanning electron microscopy (SEM) revealed evidence of reacted siliceous aggregate particles, alkali–silica gel and abundant quantities of ettringite filling the cracks and voids in the concrete. However, whereas there was firm evidence of expansion caused by ASR in the form of reacting aggregate particles with cracks emanating into the surrounding paste, there was little evidence of significant expansion of the paste due to DEF and it was concluded that ASR was the primary cause of distress and was a precursor to the subsequent precipitation of ettringite in the resulting cracks [1]. This type of ettringite formation is frequently referred to as secondary ettringite formation and is the result of the continuous dissolution of ettringite in fine cracks and voids and its reprecipitation to form

---

* Corresponding author.
E-mail addresses: mdat@unb.ca (M. Thomas), folliard@mail.utexas.edu (K. Folliard), thano.drimalas@mail.utexas.edu (T. Drimalas), terry.ramlochan@utoronto.ca (T. Ramlochan).

0008-8846/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2008.01.003

larger crystals in bigger empty spaces [2], a thermodynamically-driven spontaneous process known as Ostwald ripening. There is no evidence to suggest that this process leads to damage.

In most of the reported "cases" of DEF some other mechanism of deterioration, usually ASR, has also been present and it is difficult to determine the actual contribution made by DEF to the damage or, indeed, whether DEF played a significant role at all in the deterioration of the concrete [1,3]. Based on the number of confirmed cases of DEF damage in the field, it would appear that the risk of this process causing premature deterioration in real concrete structures is low compared to other more widespread deterioration processes. However, recently Sahu and Thaulow [4] diagnosed DEF as the sole cause of deterioration of precast concrete railroad ties (railway sleepers) in Sweden. This paper presents another such case, i.e. where DEF (in the absence of ASR) has been isolated as the sole contributory cause of premature deterioration in cast-in-place reinforced concrete bridge columns in North America.

2. Details of bridge columns

The bridge columns investigated in this study support a concrete viaduct in southern U.S.A., which was constructed in the late 1980s. Premature deterioration of the columns in the form of cracking was observed shortly before the concrete reached 10 years of age. Fig. 1 shows photographs of a typical column and the extent of cracking after approximately 15 years service. The actual dimensions of the columns and the extent of the damage varied from one column to the next, the cracking ranged from none to severe, with greater damage being observed below ground level.

Construction records, including concrete batch records, showed that, despite some variability in the materials and proportions used for different columns, the concrete typically contained a high content (~450 kg/m^3) of a high-early-strength portland cement (ASTM Type III). This, combined with the size of the columns (minimum dimension ~2 m in many cases) and the high ambient temperatures during placing, undoubtedly resulted in significant autogenous temperature rise in the concrete, and it is probable that, in a great many cases, the peak in situ temperature significantly exceeded 70 °C, which is considered by some researchers to be the minimum temperature required to initiate DEF [3,5]. Indeed, during construction it was observed that some forms warped due to the high temperatures generated in the concrete and this led to the use of fly ash in some subsequent concrete placements.

3. Forensic evaluations

The full investigation of this structure involved a comprehensive evaluation of a large number of concrete columns, both above and below ground level, using a range of different tests conducted on core samples supplemented with in situ monitoring of the columns. In this paper, only data related to the forensic evaluation conducted for four of the columns are reported.

3.1. Expansion testing of cores from laboratory-produced concrete specimens

It was proposed to conduct expansion testing of small-diameter (~50-mm) core samples from the structure immersed in: (i) hot alkaline solution to determine any residual potential expansion due to ASR and (ii) in lime-saturated water at normal laboratory temperature to examine the potential for DEF expansion. It was conjectured that storage in water would not sustain further ASR activity as the alkalis originally within the concrete would be rapidly leached out and thus be unavailable for reaction. However, this form of storage should be ideal for further expansion due to the delayed formation of ettringite, in fact, DEF might be accelerated by the reduction in pH caused by alkali leaching. Storage in hot alkaline solution (1 M NaOH at

Fig. 1. Typical appearance of columns after approximately 15 years.

Table 1
Details of laboratory expansion tests

Designation	Aggregate	Curing temp (°C)	Test solution
NR-23-LW	Non-Reactive (NR)	23	Limewater (LW)
NR-95-LW	Non-Reactive (NR)	95	Limewater (LW)
NR-23-NH	Non-Reactive (NR)	23	Sodium Hydroxide (NH)
NR-95-NH	Non-Reactive (NR)	95	Sodium Hydroxide (NH)
RS-23-LW	Reactive Sand (RS)	23	Limewater (LW)
RS-95-LW	Reactive Sand (RS)	95	Limewater (LW)
RS-23-NH	Reactive Sand (RS)	23	Sodium Hydroxide (NH)
RS-95-NH	Reactive Sand (RS)	95	Sodium Hydroxide (NH)

80 °C), on the other hand, would obviously promote continued ASR, but potentially inhibit further expansion due to DEF due to the high temperature and pH. Famy et al. [6] showed that storage of heat-cured mortar bars in solution containing KOH resulted in either a postponement or an elimination of expansion, depending on the pH of the solution.

In order to test this hypothesis, two concrete mixes were produced with high-early-strength cement known from previously tests by the authors to produce DEF expansion in heat-cured mortars subsequently stored in water at laboratory temperature. The concrete contained 420 kg/m^3 of high-alkali cement raised to 1.25% Na_2Oe with the addition of NaOH to the mix water producing a total alkali content of 5.25 kg/m^3 Na_2Oe. One mix was produced with a highly-reactive sand and the other with non-reactive aggregates. A number of 150 × 300 mm concrete cylinders were cast from each mix and the cylinders were either initially cured under normal laboratory conditions or were exposed to a heat-curing regime with a maximum peak temperature of 95 °C. After initial curing, cylinders were stored in sealed containers over water at 38 °C. After 150 days storage, cracking was observed on both the non-heat-cured and heat-cured concrete containing reactive sand. At this time, 50-mm diameter cores were cut from cylinders, stainless steel pins (for expansion measurements) were embedded into the end of the cores, and the cores were stored in either lime-saturated water at room temperature or in 1 M NaOH at 80 °C. This resulted in eight different combinations of aggregate, curing temperature and test solution as shown in Table 1.

The expansion of concrete cores stored in limewater and NaOH solutions are shown in Fig. 2. Only the cores that were heat-cured expanded during storage in limewater, non-heat-cured cores with reactive aggregate did not expand. This confirms the hypothesis that storage of small-diameter cores in water does not sustain continued ASR due to the leaching of alkalis. Only the cores that contained reactive aggregate expanded during storage in 1 M NaOH at 80 °C, heat-cured cores with non-reactive aggregates did not expand confirming the inhibiting effect of high temperature and high pH on expansion due to DEF.

3.2. Details of columns investigated

Concrete cores (100-mm and 50-mm diameter) were extracted from four of the columns and these are designated as columns A, B, C and D for the purposes of this paper. Column C showed no unusual premature deterioration. Columns A and D were extensively cracked, whereas Column B exhibited somewhat reduced damage compared to A and D. Column A is the largest column being approximately 2 × 2 m in cross section. Columns B and C have a cross-sectional area that is approximately 40% smaller than column A. The dimensions of column D were not known at the time of writing but it has approximately the same cross-section as column A.

3.3. Alkali-content of concrete cores

The water-soluble alkali content of concrete cores were measured using a hot-water extraction method. Briefly, this method involves immersing a 10-g powdered sample of concrete in 100 mL of distilled water, boiling the water for 10 min and then allowing it to stand overnight. The sodium and potassium in solution are then determined by flame photometry.

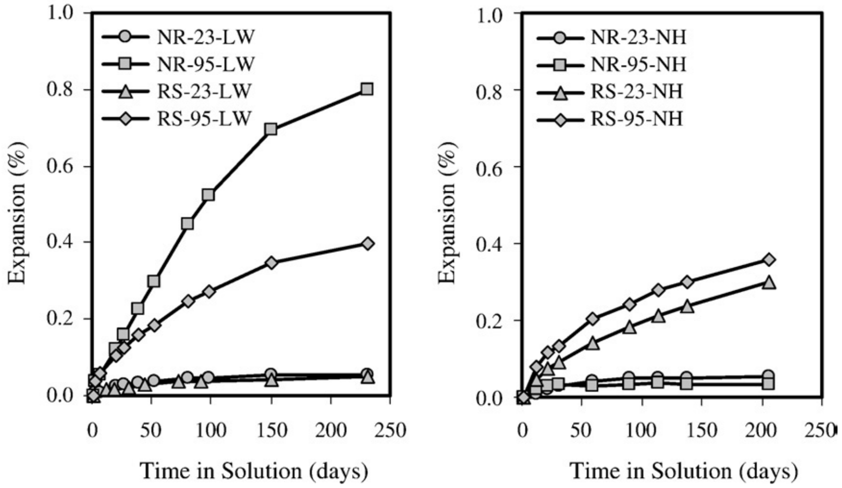

Fig. 2. Expansion of 50-mm cores cut from laboratory-produced concrete cylinders and stored in limewater (left) and NaOH solution (right).

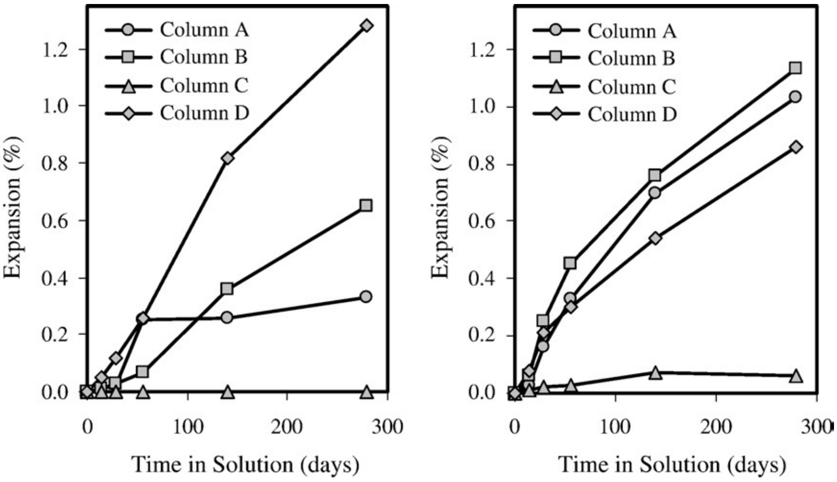

Fig. 3. Expansion of 50-mm cores cut from concrete columns and stored in limewater (left) and NaOH solution (right).

3.4. Expansion testing of cores from concrete columns

Expansion tests were conducted on either 50-mm cores taken directly from the structure or 50-mm cores cut from larger (100-mm) cores. Stainless steel pins were embedded in the ends of cores, which were trimmed to provide a gauge length of 250 mm. The expansion results for cores stored in limewater at laboratory temperature and 1 M NaOH at 80 °C are shown in Fig. 3; the results shown are, in most cases, the average of at least two cores.

Cores from Columns A, B and D all showed very significant expansion when stored in limewater at normal laboratory temperature, indicating a substantial potential for further DEF. Cores from the same structures also showed expansion in 1 M NaOH at 80 °C indicating the presence of reactive silica and potential for ASR if sufficient alkali remains in the concrete. Cores from Column C show little or no expansion in either environment suggesting that there is no potential for DEF or ASR in this concrete.

3.5. SEM investigations

Polished samples prepared from cores taken from all four columns were examined by scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDXA). Table 2 presents a summary of the findings from the SEM-EDXA investigation. Included in Table 2 is a visual rating based on the damage observed in the field and the results of tests to determine the water-soluble alkali content of the concrete. Column C exhibited no significant damage or evidence of either ASR or DEF. This may be attributable to the presence of fly ash which is known to be effective in controlling both ASR and DEF provided it is used in sufficient quantity. The other three columns did not contain fly ash; damage caused by DEF was detected in all three of these columns, but evidence of ASR was only found in two of the columns (B and D). The aggregates used appear to be similar in composition and, hence, the absence of ASR in Column A may be a result of the concrete having lower alkali content compared with Columns B and D (although the differences are not large). The expansion testing of cores (Fig. 3) indicate that the aggregate in Column A is potentially reactive and produces damaging reaction when provided with sufficient alkalis.

Fig. 4 is a back-scattered electron (BSE) image showing the extent of the damage present in Column A, for which DEF appears to be the sole distress mechanism. Extensive cracking was observed around aggregates and through the paste, with occasional cracking through aggregate particles. Many of the cracks were filled with ettringite. Similar damage was observed on Column D (Fig. 5) and, to a lesser extent, Column

Table 2
Summary of findings for concrete columns

Column	Field damage[a]	Alkali content[b] (kg/m^3 Na$_2$Oe)	ASR detected	DEF detected	Fly ash detected
A	Severe	2.32	No	Yes	No
B	Moderate	3.17	Yes	Yes	No
C	None	5.25	No	No	Yes
D	Severe	2.69	Yes	Yes	No

[a] Based on visual examination of structures in the field (above ground level).
[b] Water-soluble alkali.

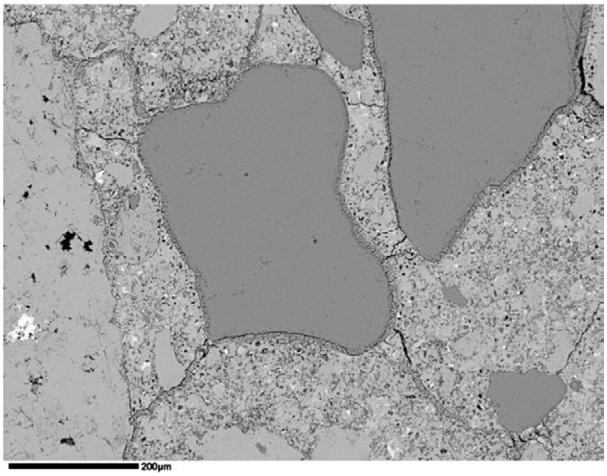

Fig. 4. BSE image of polished sample from Column A.

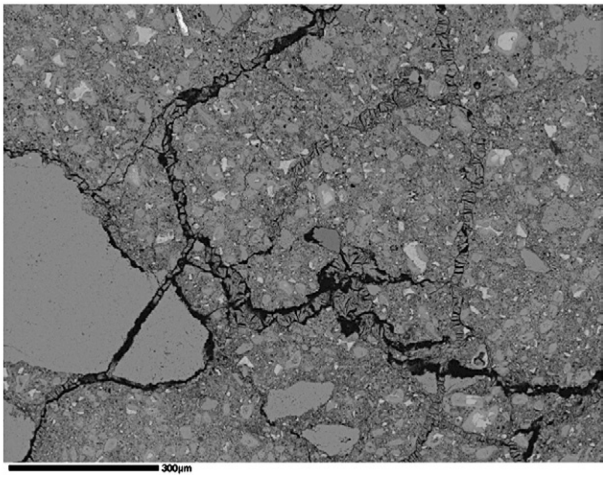

Fig. 5. BSE image of polished sample from Column D.

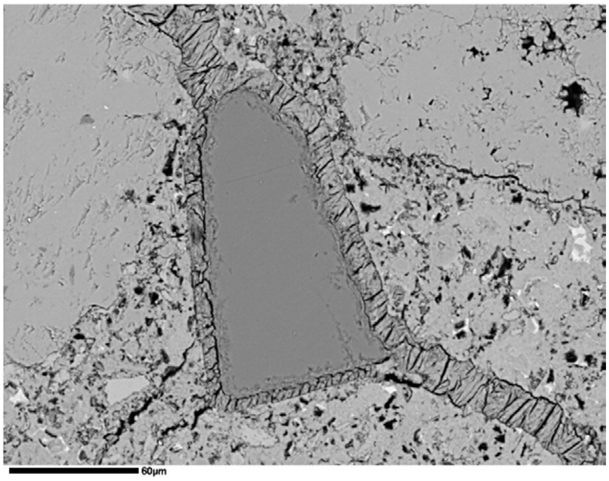

Fig. 7. BSE image of polished sample from Column A showing ettringite-filled gap around aggregate particle.

B, although both of these columns showed some signs of ASR damage, including cracks through aggregate particles, some of which were partially filled with alkali–silica gel.

Fig. 6 shows a BSE image from Column 3. The spherical fly ash particles are easily detected in this image. Although there is no evidence of significant damage caused by either ASR or DEF, there is abundant ettringite present in the sample filling the voids and entrained air bubbles. Microanalysis of the residual fly ash indicates the ash to have a moderate calcium content, however, analysis of fly ash in hydrated concrete is complicated by the fact that much of the fly ash has hydrated and the chemical composition of the residual material may not be representative of the bulk material.

As discussed earlier, the presence of ettringite in cracks and voids in concrete is not sufficient evidence that delayed ettringite formation, or indeed another form of sulfate attack, has occurred. DEF results in an expansion of the cement paste and the increase in volume of the paste in relation to the (presumably volumetrically-stable) aggregates should result in a separation between the two or, in other words, "gaps" opening between the paste and aggregate. This feature was frequently found in the specimens prepared from Columns A, B and D. Figs. 7 and 8 show typical examples of this occurrence. In both of these examples the gap between the cement and aggregate has been filled with ettringite. In Fig. 7, from Column A, there is no sign of aggregate reactivity, whereas in Fig. 8, from Column B, significant reaction of the aggregate has occurred.

Fig. 9, from Column A, is a BSE image with X-ray maps for sulfur, sodium and potassium. These images show the presence of a complete "ring" of a sulfate-bearing mineral (ettringite) around a siliceous aggregate particle, with no associated alkali–silica reaction products (sodium and potassium are only visible in the feldspar-containing particle to the left). The features shown in Figs. 7–9 are, in the authors' opinion, reliably diagnostic features of DEF.

As shown in Fig. 3, cores from Columns A, B and D underwent substantial damage when stored in limewater at normal laboratory temperature. After prolonged storage, in many cases,

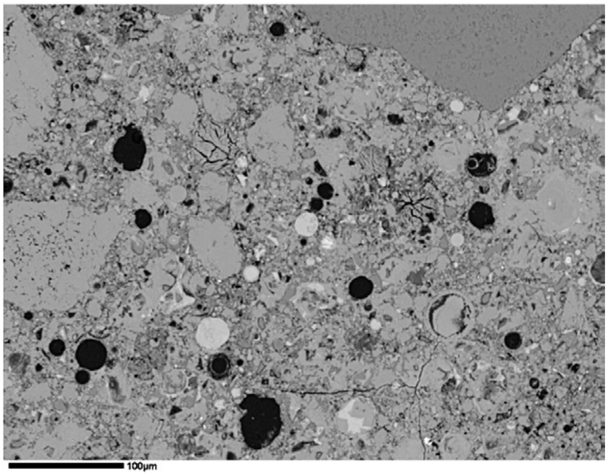

Fig. 6. BSE image of polished sample from Column C.

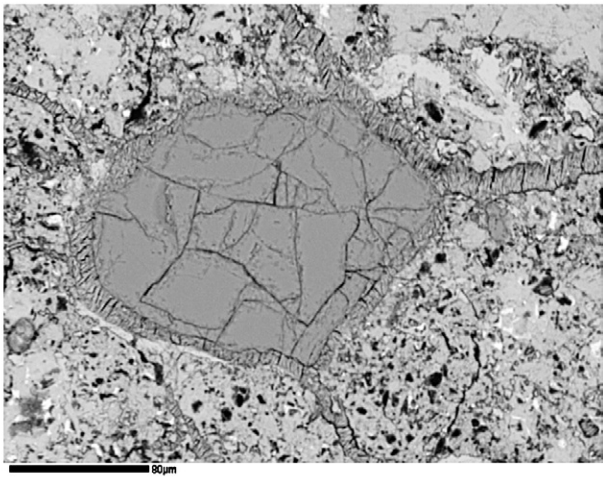

Fig. 8. BSE image of polished sample from Column B showing ettringite-filled gap around reacting aggregate particle.

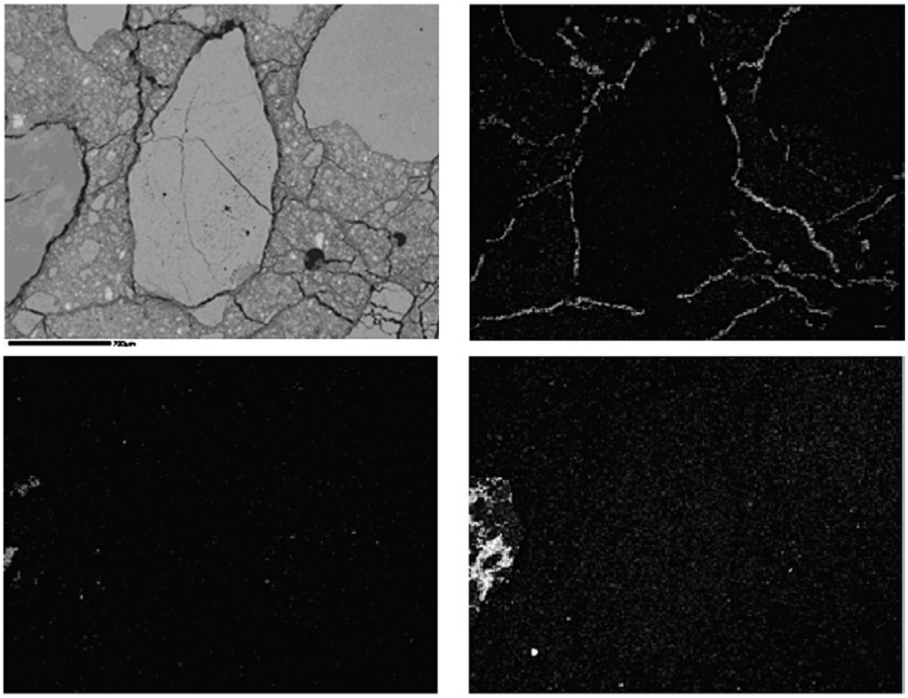

Fig. 9. BSE image and X-ray maps for sulfur (top right), sodium (bottom left) and potassium (bottom right) from Column A.

aggregate particles on the cut surface of cores became detached leaving empty sockets, presumably as the paste around the aggregate expanded. Also, visible gaps were observed (without the aid of microscopy) to open around some aggregate particles. Fig. 10 shows a sawn surface of a 50-mm diameter core (from Column A) after immersion in limewater. Gaps around aggregate particles are clearly visible. Fig. 11 shows a scanning electron (SE) image of a socket left after an aggregate particle became detached from the surface of a core (from Column B) during immersion in limewater. The image clearly shows the formation of abundant ettringite at the cement-aggregate interface.

4. Discussion

There have been relatively few documented cases where the process of DEF has been unequivocally established as a cause of damage to concrete structures and in most of these cases other deterioration processes (particularly ASR) have also contributed to the observed distress [1,3,7]. Of the three damaged concrete columns investigated in this study, two of them were affected by both DEF and ASR. However, in one column (designated as Column A) DEF appears to have been the sole cause of distress. This is of particular interest as the concrete was cast in place and no external heat-curing was applied. Of course, the use of a high amount of high-early-strength cement, the size of the columns and the high ambient temperatures at the time of casting would be expected to lead to high internal concrete temperatures shortly after casting. In massive sections where there is a slow rate of heat loss, the temperature rise can be estimated to be in the region of 12 °C per 100 kg/m^3 of cement [8,9], which would result in a temperature rise of approximately 54 °C in a concrete with 450 kg/m^3 of cement. Depending on the temperature of the concrete at the time of placing, the maximum internal temperature would almost certainly exceed 70 °C and possibly even 80 °C.

Although there is no evidence of ASR damage in Column A, the coarse and fine aggregates appear to be of similar composition to those used in the other columns, two of which (Columns B and D) showed signs of deleterious reaction. It is possible that the absence of damaging reaction is attributable to the lower alkali content in the concrete of this column compared to the others (see Table 2). Despite the absence of damaging reaction, it is still possible that some reaction between the alkalis in the pore solution and the reactive silica in the

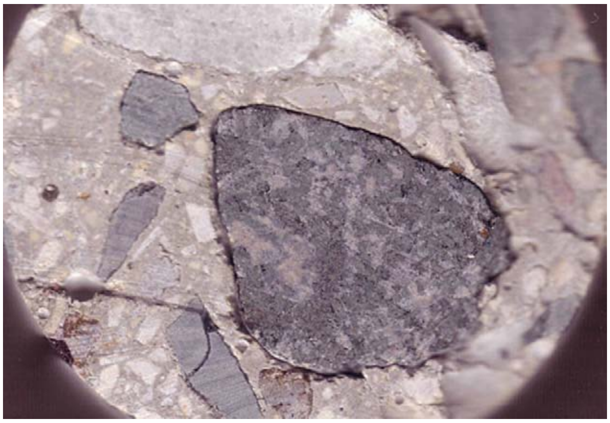

Fig. 10. Photograph of sawn surface on 50-mm diameter core from Column A after immersion in limewater.

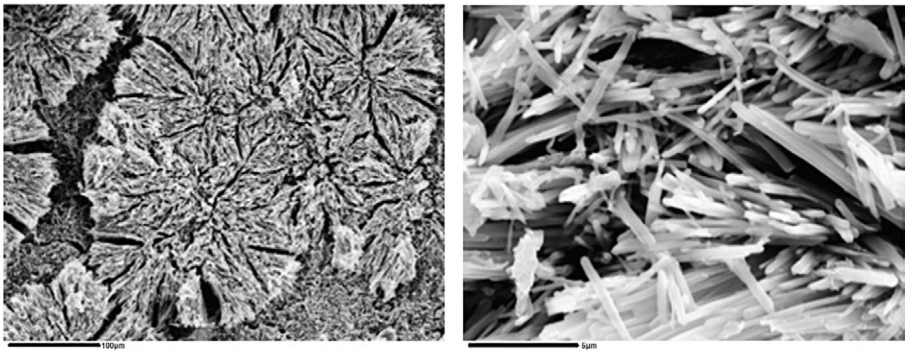

Fig. 11. SE image of aggregate socket on fracture surface from Column B after immersion in limewater.

aggregates occurred, resulting in a reduction in the pore solution pH. It has been suggested that the reduction in pH that occurs as a result of either leaching (Famy et al., 2001) or reaction of alkalis (ASR) leads to the release of the sulfates that were encapsulated in the C-S-H during early hydration at elevated temperature, thereby triggering DEF. The absence of damaging ASR or DEF in Column C is likely due to the presence of fly ash. It is well documented that fly ash can control ASR expansion, although its efficacy in this role depends on the composition of the ash and the amount present (among other factors). Neither the composition nor the amount of fly ash used was determined in this study. A sufficient quantity of fly ash will also control expansion caused by DEF (Ramlochan et al., 2003). This could result from the reduction in the peak temperature of concrete containing fly ash, although sufficient quantities of fly ash have been found to be effective in controlling DEF expansion even when the peak temperature during curing reaches 95 °C due to the application of external heat (Ramlochan et al., 2003).

The role of DEF was readily diagnosed in these concretes owing to the presence of ettringite-filled gaps around many aggregate particles. In Column A, the contribution of DEF to the observed damage was easy to determine because of the absence of any other form of deterioration. However, in some cases reliably diagnostic features may not be so evident and, even when they are present, the contribution of DEF may be difficult to separate from the actions of other mechanisms (e.g. ASR in the case of Columns B and D). Soaking small-diameter cores in water can provide useful information on the role of DEF and the potential for further damage. Of course, expansion of such cores may be caused by other processes (e.g. internal sulfate attack due to the presence of excess sulfate in the concrete ingredients, unsoundness arising from the presence of excessive amounts of free MgO or CaO, alkali–carbonate reaction) and microscopical investigations would be required to completely eliminate any contribution from these distress mechanisms.

5. Conclusion

Delayed ettringite formation was confirmed as the sole cause of distress in one cast-in-place concrete column and as a contributory cause in two other columns. The action of damaging DEF was readily established by the presence of numerous aggregate particles completely surrounded by ettringite-filled gaps. Small-diameter (50-mm) cores drilled from the concrete showed significant expansion (0.3 to 1.3%) when immersed in limewater at normal laboratory temperature. Laboratory tests showed that these storage conditions would not sustain continued expansion due to ASR.

References

[1] M.D.A. Thomas, T. Ramlochan, Diagnosing the cause of deterioration in prestressed concrete beams—ASR or DEF? Proceedings of the 8th Euroseminar on Microscopy Applied to Building Materials, 2002, pp. 289–296.

[2] V. Johansen, N. Thaulow, J. Skalny, Simultaneous presence of alkali–silica gel and ettringite in concrete, Advances in Cement Research 5 (17) (1993) 23–29.

[3] M.D.A. Thomas, Delayed ettringite formation: recent developments and future directions, in: S. Mindess, J. Skalny (Eds.), Materials Science of Concrete VI, American Ceramics Society, Westerville, OH, 2001, pp. 435–482.

[4] S. Sahu, N. Thaulow, Delayed ettringite formation in Swedish concrete railroad ties, Cement and Concrete Research 34 (2004) 1675–1681.

[5] T. Ramlochan, P. Zacarias, M.D.A. Thomas, R.D. Hooton, The effect of pozzolans and slag on expansion of mortars cured at elevated temperature: Part 1: Expansive Behaviour, Cement and Concrete Research 33 (2003) 807–814.

[6] C. Famy, K.L. Scrivener, A. Atkinson, A.R. Brough, Influence of the storage conditions on the dimensional changes of heat-cured mortars, Cement and Concrete Research 31 (2001) 795–803.

[7] M.D.A. Thomas, T. Ramlochan, Field cases of delayed ettringite formation Internal Sulfate Attack and Delayed Ettringite Formation, in: K. Scrivener, J. Skalny (Eds.), Proceedings of an International RILEM Workshop on Internal Sulfate Attack and Delayed Ettringite Formation, RILEM Publications SARL, 2004, pp. 85–97.

[8] M.E. FitzGibbon, Large pours for reinforced concrete structures, Concrete 10 (3) (1976) 41.

[9] M.E. FitzGibbon, Large pours—2, heat generation and control, Concrete 10 (12) (1976) 33–35.