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Delayed ettringite formation in Swedish concrete railroad ties

Sadananda Sahu*, Niels Thaulow

RJ Lee Group, Inc., 350 Hochberg Road, Monroeville, PA 15146, USA

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Abstract

A petrographic examination of cracked Swedish concrete railroad ties identified delayed ettringite formation (DEF) as the damaging mechanism. This was unexpected because the concrete railroad ties were steam-cured with a maximum concrete temperature below 60 °C. The consensus in the published literature is that DEF only occurs in concrete subjected to heat curing above 70 °C. However, DEF is not only influenced by the curing temperature, but also by various other factors, such as cement composition (alkalis, C_3S, C_3A, SO_3, and MgO), fineness, etc. If an unfavorable combination of these parameters exists, delayed ettringite may occur at lower temperatures than 70 °C.

In this paper, the influence of various parameters on DEF is discussed with reference to the investigated concrete.

Keywords: Delayed ettringite formation (DEF); Temperature; Petrography; SEM; Concrete

1. Introduction

Since the 1970s, failures of a number of precast concrete products manufactured at elevated temperatures have been reported. They have been characterized by cracking after several years of service in environments exposed to weather. This type of phenomenon notably occurs, although not exclusively, in railway ties. The pioneering work of Ludwig et al. [1–3], later confirmed by other researchers [4–8], has shown that ettringite, one of the initial hydration products formed during the hydration process of Portland cement prior to curing at a temperature of 70 °C or above, is destroyed during heat treatment and further formation of ettringite is inhibited. During this process, a significant amount of sulfate is absorbed in the C-S-H or present in the pore solution [9,10]. Some authors believe that monosulfate is the stable phase under these conditions and is intermixed with C-S-H [7]. The subsequent formation or reformation of ettringite during the service life of the concrete at ambient temperature and exposure to moisture is known as delayed ettringite formation (DEF).

Mechanism(s) for DEF and the cause(s) of expansion are not agreed upon by all researchers [11,12]. In fact, DEF is a controversial subject of great concern for all parties involved. Investigations have been performed by many researchers and various overviews of DEF have been reported [2–14]. Despite considerable research efforts, the mechanism(s) of DEF is not completely understood, and detailed explanation of the physical and chemical aspects of the expansion has not been thoroughly documented.

A number of railroad ties used in Sweden have shown premature deterioration. The ties were produced in the period of 1992 to 1996 and were in service since then. During the winter of 1999, visible map cracking (see Fig. 1) was observed in a small percentage of ties manufactured by the same plant. The manufacturing process was the same in all the time of production. Particularly, the steam-curing temperature regime was constant all the time.

In this investigation, samples from the visibly uncracked and cracked ties were examined by pertrographic methods.

2. Experimental

The as-received samples were examined visually and by stereo-optical microscopy to ascertain the nature of cracking and look for signs of deposits. White deposits were observed in the air voids of cores obtained from the cracked sleeper. The white deposits were scraped and

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* Corresponding author. Tel.: +1-724-325-1776; fax: +1-724-733-1799.

E-mail address: ssahu@rjlg.com (S. Sahu).

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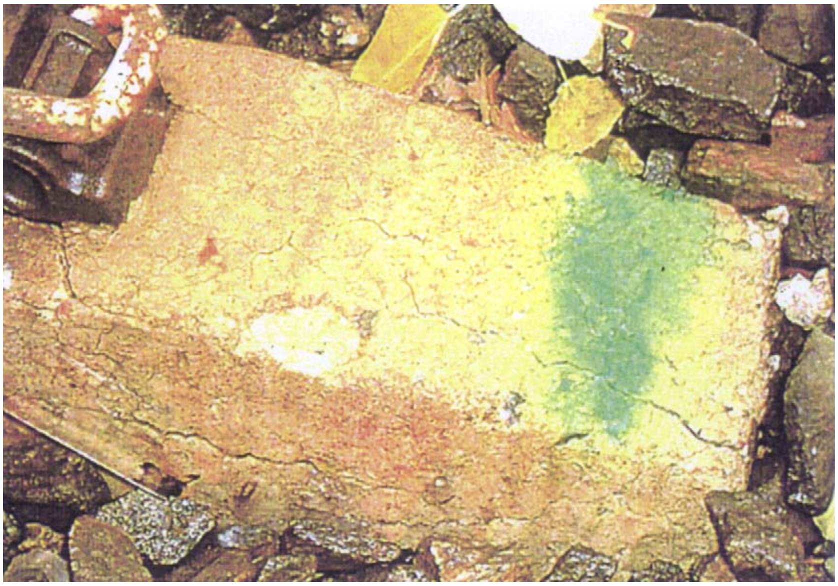

Fig. 1. Map cracking on the shoulder of a railroad tie.

spread over an adhesive strip, which was then carbon-coated and analyzed using a scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS).

A vertical slice was cut from near the middle of each concrete core and divided into three sections, top (T), middle (M), and bottom (B). One and one-half inch size samples were cut from the top and middle and polished thin sections were prepared for analysis by optical microscopy. The specimens were dried under vacuum and were vacuum-impregnated using a low-viscosity epoxy resin with fluorescent dye and were cured. The specimen blocks were mounted on glass slides by using glue. After hardening of the glue, the sample was cut leaving less than 1-mm-thick concrete on the glass surface. The impregnated sample was then ground using silicon carbide slurries between 600 and 1000 grit on a glass plate to the required thickness of about 25 μm. A final polish was obtained using 9 to 1/4 μm diamond paste on a cloth. The thin sections were used for an optical microscopy study. After optical microscopic study, the polished surfaces were coated with a thin layer of carbon by evaporative deposition. The carbon-coated samples were further used for backscattered electron mode SEM analysis coupled with EDS.

3. Results

Petrographic observations of a cracked as well as an uncracked tie are presented in separate sections below.

3.1. Cracked railroad tie

During visual examination, white deposits were observed in the air voids on the surface of the core. The white deposits were analyzed using SEM–EDS. Analysis showed well-developed needle-like crystals of ettringite (Fig. 2).

Polarized light microscopic analysis indicated that the coarse aggregate used in this concrete is crushed granite rock. The fine aggregate is manufactured sand. No signs of alkali–silica reaction (ASR) were observed in any of the samples.

Furthermore, SEM–EDS analysis indicated massive deposits of ettringite at the paste/aggregate interface (Fig. 3). The air void in the image of Fig. 3 is also filled with

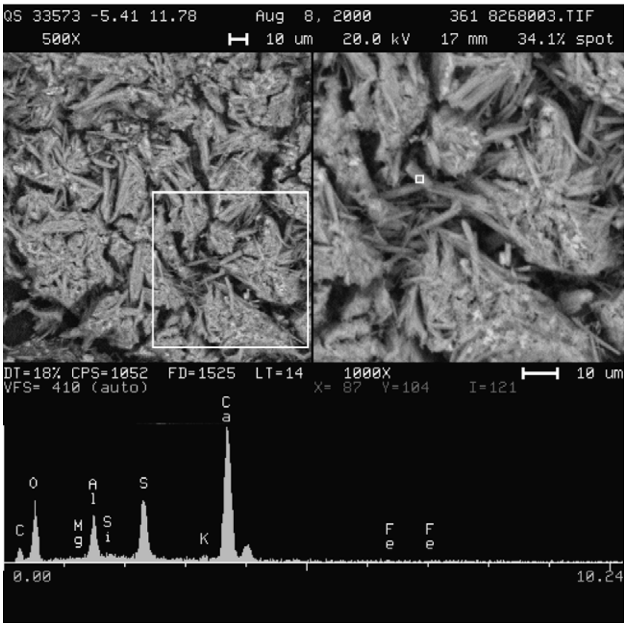

Fig. 2. Morphology and chemical composition of the white deposits in air voids identified as ettringite. The sample is from a cracked railroad tie.

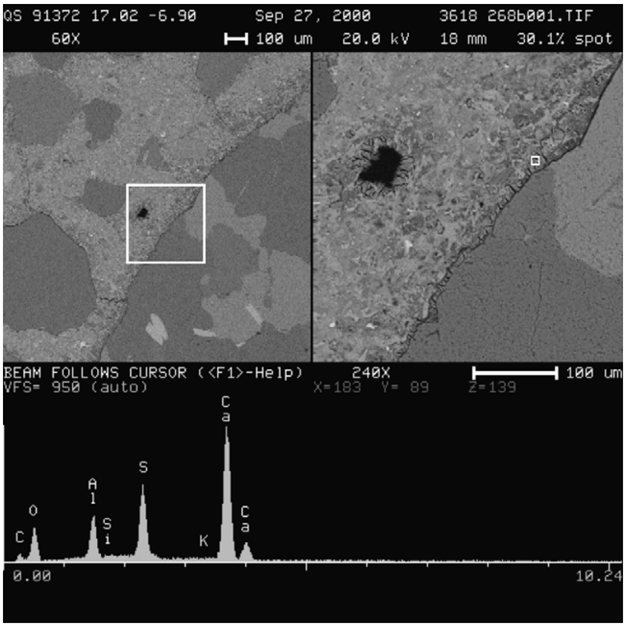

Fig. 3. Ettringite deposits at the paste/aggregate interface. Shoulder of the cracked tie.

ettringite. Imaging the paste microstructure at relatively higher magnification shows significant ettringite deposits in the micropores and former cement grains (Fig. 4). Formation of two-toning of the C-S-H was observed (Fig. 5). The right image of Fig. 5 shows a completely hydrated cement grain with a brighter outer rim followed by a darker inner rim and deposits of ettringite at the center of the grain.

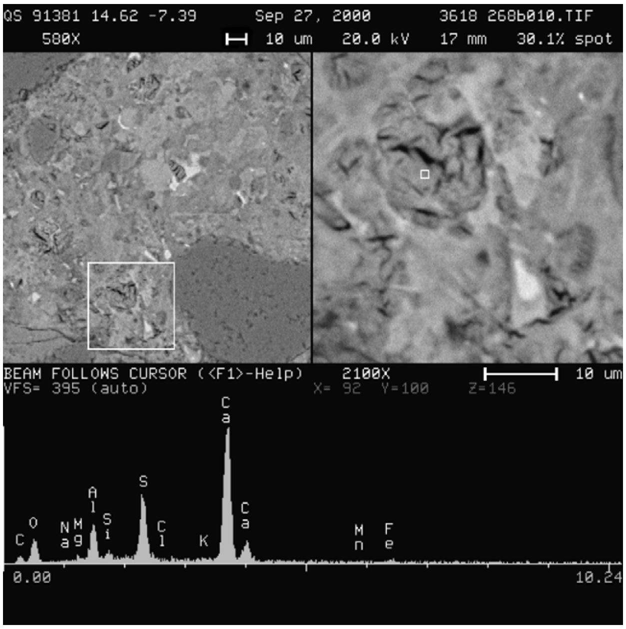

Fig. 4. Ettringite deposits in the paste. Shoulder of the cracked tie.

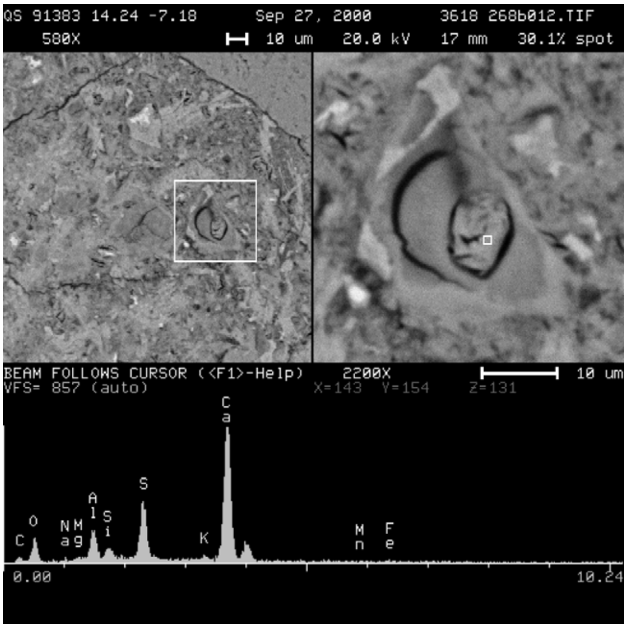

Fig. 5. Ettringite deposit in a former cement grain. Two-toned structure of a hydrated cement grain is observed. Shoulder of the cracked tie.

These observations suggest that the cause of map cracking is DEF. The cracks are not confined to the surface only, but they are deep into the concrete.

The observation of DEF prompted an investigation of the details of the tie production process, the type of cement used and mix design of the concrete. The cement used in the tie production is a special type of Portland cement. The chemical composition of the cement is provided in Table 1. The chemical composition indicates a high alkali-, sulfate-, and C_3A-content cement. Additionally, the fineness of the cement is quite high. The cement content of the concrete was relatively high in the range of 470 kg/m^3 (8.4 $sacks/yd^3$) to 520 kg/m^3 (9.3 $sacks/yd^3$). The water–cement ratio was 0.40. A superplasticizer was used. The review of production records indicated a 12-h curing in mould in a humid chamber followed by a 5-h steam curing with maximum temperature inside the concrete below 60 °C. The temperature rise of the concrete with time is plotted in Fig. 6.

Table 1
Composition of the cement used in the tie manufacture

C_3S (wt.%)	59
C_3A (wt.%)	8
Al_2O_3 (wt.%)	4.4
MgO (wt.%)	3.5
SO_3 (wt.%)	3.7
Na_2O_{eq} (wt.%)	1.16
SO_3/Al_2O_3 (wt./wt.)	0.84
Fineness (m^2/kg)	550

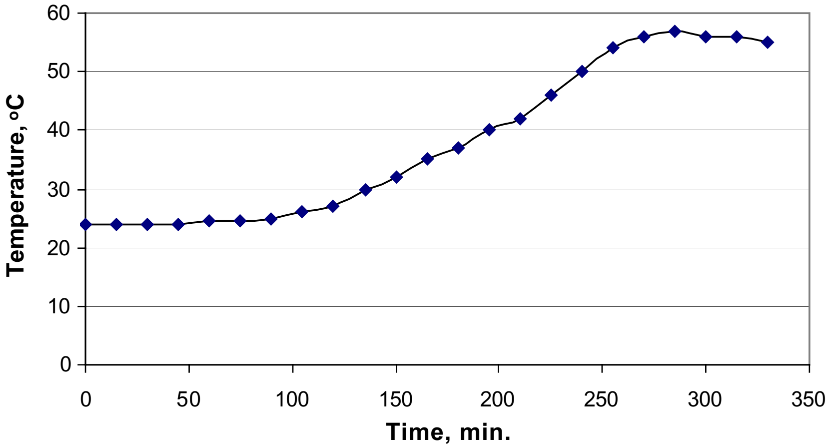

Fig. 6. Concrete temperature during steam curing as measured inside the concrete tie.

3.2. Uncracked railroad tie

Using the same aggregates, cement, superplastcizer, mix design and curing regime, new railroad ties were made. These ties were never put in service. After about 3 months, cores from the shoulder and center were obtained and analyzed.

SEM–EDS analysis of the inner hydration product indicates the presence of elevated levels of sulfur (Fig. 7). Similarly, elevated levels of sulfur and potassium were observed in the outer hydration product (Fig. 8). A significant amount of unhydrated cement grains was observed in this sample.

4. Discussion

The microstructure of concrete exhibiting distress from DEF is characterized by cracks and gaps at the paste/aggregate interface. Factors that influence DEF include the following: elevated curing temperature, alkali content of cement, fineness of cement, C_3S content of cement, C_3A content of cement, C_4AF content of cement, SO_3 content of cement, MgO content of cement and exposure to moisture.

4.1. Temperature

There is a common understanding among the researchers that DEF can only occur in elevated temperature-cured

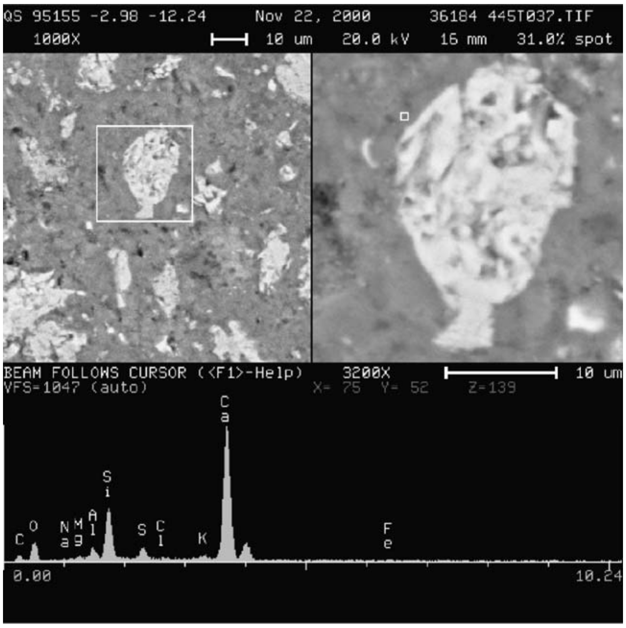

Fig. 7. Sulfur enrichment in the inner hydration product. This tie was never exposed to the service conditions.

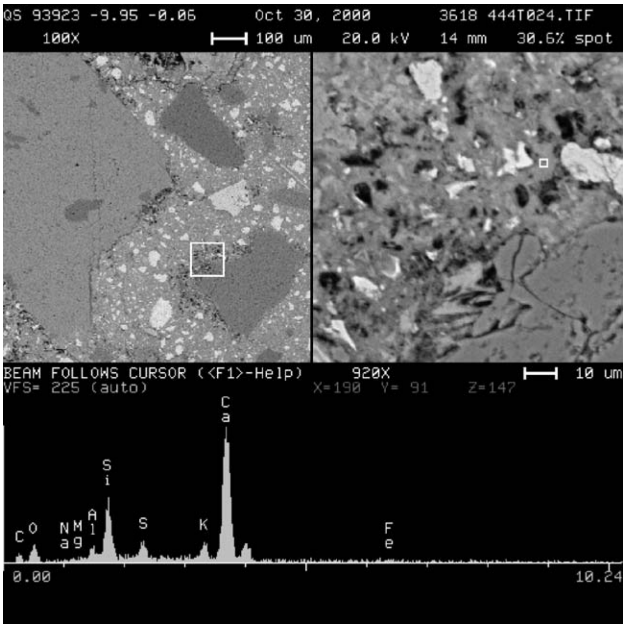

Fig. 8. Enrichment of sulfur and potassium in the outer hydration product. This tie was never exposed to the service conditions.

concrete. There are many authors who suggest that heat treatment of concrete at 70 °C or above is a necessary condition for DEF [2–6]. Recently, there are some reports suggesting that DEF can form in concrete not subjected to elevated temperature curing [15–17]. The cause is attributed to elevated clinker sulfate and its slow release from the clinker minerals [15,16] or combination of high clinker sulfate and total sulfate in the cement [17]. However, existence of ambient temperature DEF is disputed [18].

Kelham [19,20] established an empirical relation between the composition of cement and the risk of expansion at 90 °C.

This empirical equation is not able to establish what happens for a given cement high in specific surface area, C_3S, MgO, Na_2O, SO_3, and C_3A content, if the temperature is lowered or increased from 90 °C. This empirical equation was arrived at measuring the expansion of mortar bars. However, experimental data show that for the same cement, by lowering the curing temperature, the occurrence of DEF and expansion can be delayed much longer [21].

Another empirical relation was proposed by Lawrence [5]. The concrete was subjected to temperatures of 100 °C and after 800 days in water, the expansion was measured. Similarly, this equation does not evaluate the effect of various curing temperatures. The equation proposed by Hobbs [22] has a similar problem.

None of the empirical equations takes into account the variation in curing temperature or the cement content.

Sulfate adsorption from internal sources may occur during formation of C-S-H gel. C-S-H gel will adsorb sulfate faster at high temperatures and then desorb sulfate slowly at normal temperatures [23–25]. Slow release of sulfate from an internal source may be a critical condition for DEF in elevated temperature-cured Portland cement concrete. A publication that explains the relationships between elevated temperature curing and pore solution chemistry of Portland cement was published in 1992 by Wieker et al. A summary of their observations is as follows [21]:

1. With increasing temperature, the pore solution at the end of the heat treatment gets higher in SO_4^{2-} and lower in OH^- concentration. These two contrarily running changes in the concentration of OH^- and SO_4^{2-} ions are intensified by a higher alkali content as well as by a higher molar SO_3/Al_2O_3 ratio of the cement.
2. Storage of heat-treated samples at room temperature under humid conditions results in an inversion of the concentration changes observed during heat treatment. That means lowering of the SO_4^{2-} and increase of the OH^- concentration in the pore solution.
3. The decrease in SO_4^{2-} concentration is connected with a secondary formation of ettringite, which was decomposed during the treatment at temperatures between 50 and 80 °C.

An increase in sulfate-rich pore solutions is observed with increased temperature. A distinct break is not observed with increased temperature, therefore indicating a process that may be continuous and not beginning at a specific temperature. A decrease in sulfate and an increase in hydroxide concentrations are observed over time. When considering these factors, it could be expected that expansion may occur at lower temperatures than 80 °C but that the process may occur at a time period longer than 300 days.

4.2. Alkali content

An elevated alkali content of cement can retard or inhibit the normal progression of primary ettringite formation. Potassium hydroxide has been shown to accelerate the hydration of C_3S and retard ettringite formation [26]. Therefore, C-S-H formation is more extensive during the period when the alite and belite phases are undergoing hydration. The retardation of ettringite formation and the acceleration of C_3S hydration by temperature and alkalis provide a mechanism by which sulfate may become incorporated into the C-S-H gel and not form ettringite. Glasser [27] stated “at 50 °C and especially at 85 °C the soluble sulfate component of the pore fluid increases rapidly, even more so as the alkali concentration increases.”

In addition, research related to C-S-H and sulfate related to temperature and basicity was conducted by Diviet and Randriambololona [28]. The following conclusions were made, “The capacity of adsorption of SO_4^{2-} ions on C-S-H is high and depends on the basicity of the pore solution of the concrete and on the temperature to which the concrete structure is subjected. A higher pH and temperature favor adsorption. The adsorption of SO_4^{2-} ions on C-S-H is reversible.”

Therefore, elevated curing temperatures and increased alkali content in cement result in sulfate-rich C-S-H gel and calcium hydroxide as the hydration products. In this situation, any change in the conditions that promote a supersaturation of pore solution with respect to ettringite lead to DEF. Lowering the temperature to ambient is a situation, where ettringite becomes the stable phase and is formed from a supersaturated solution with sulfate being supplied by the C-S-H gel. A drop in pH due to ASR or carbonation may also promote DEF. Diamond and Ong [10] stated: in “alkali–silica reaction: loss of alkali from solution due to alkali–silica reaction could lead to a situation in which ettringite formation is preferential at selected locations due to locally depressed pH and alkali concentration due to the formation of alkali–silica reaction gel.”

A study by Lagerblad and Utkin [29] using two different cements shows that the high alkali-content cement (Na_2O eq. = 1.13) expanded significantly due to DEF at 75 °C within a year. The study shows that by lowering the temperature from 95 to 75 °C, the expansion is delayed. After 1 year of expansion measurements, the authors concluded that expansion only occurs if heat-treated above 60

°C. It seems that expansion would have occurred in the concrete heat-treated at 60 °C, after several years, if the measurements had been continued.

Another empirical relation established by Zhang et al. [30] shows that the DEF index is directly related to the square root of the total alkali content of the cement.

Review of these literatures suggest that DEF is possible in a concrete steam-cured below 70 °C if elevated levels of alkalis are present in the cement.

4.3. Other factors

Other factors that influence DEF include cement parameters, such as fineness, C_3S, C_4AF, C_3A, MgO, as well as permeability and environmental conditions. Cement fineness controls the specific surface area and thus influences early hydration rates. In addition, increased temperature accelerates C_3S hydration rates. Microanalysis indicates that the increased growth rate of the C-S-H paste tends to trap sulfate ions in the C-S-H gel. The release of sulfate ions to the pore liquid phase and aluminate from other slowly hydrating cement phases, such as C_4AF, are present together with calcium and OH^- ions. Ettringite may then precipitate under supersaturated conditions. This delayed ettringite may be expansive and may provide a mechanism for expansion and cracking of the paste. Permeability through porosity and preexisting cracks increases the rate of the process by allowing moisture to penetrate into the paste microstructure.

5. Conclusions

1. The cracked concrete railway tie has been damaged due to DEF occurring at temperatures lower than expected.
2. The unusual and unexpected combination of the following factors may have caused DEF to occur just below 60 °C: high cement content in the concrete, cement with high specific surface, high alkali content, high sulfate content, high magnesium oxide content in the cement, and high reactivity of the ferrite phase in the cement.
3. We see evidence that the young, uncracked tie will develop damage due to DEF in the future, if exposed to moisture.
4. The literature survey suggests that a potential for DEF exists at temperatures below 70 °C if certain conditions are satisfied (e.g., the use of high alkali cement with high surface area, high C_3S content, concrete with low water-to-cement ratio and high cement content).

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