Committee Report: JCI-TC173A

Technical Committee on Delayed Ettringite Formation

Shunsuke HANEHARA[*1], Yuichiro KAWABATA[*2], Shoichi OGAWA[*3], Hikotsugu HYODO[*4] and Natsuki YOSHIDA[*5]

Abstract

When moisture is supplied after hardening of high-temperature cured concrete, the concrete has a risk to expand owing to re-formation of ettringite (delayed ettringite formation: DEF). Presently, findings for DEF have not been fully organized, and the risk of deterioration due to DEF in structures in Japan, in particular, remains unclear. In this technical committee, regarding expansion due to DEF and the resulting deterioration in structures, we comprehensively summarized the mechanisms and diagnosis procedures, comparisons between overseas structures and domestic structures, and preventive measures for structures. Although domestic examples of DEF-related deterioration in structures are limited, regarding the risks thereof, we report the results of discussions from the viewpoints of material science and structures.

Keywords: ettringite, delayed formation, expansion, risk, mechanism, diagnosis

1. Introduction

Ettringite (Ett) re-formation is a phenomenon in which concrete expands when moisture is supplied after hardening to high-temperature cured concrete [1)]. Examples of this have been recently reported in mass concrete and other structures overseas[2)]. This phenomenon is referred to as delayed ettringite formation (DEF), and although no cases of structures that have deteriorated considerably due to DEF have been reported in Japan, the possibility of such deterioration has been indicated[3)4)]. Expansion due to DEF is assumed to involve large expansions due to an alkali–silica reaction (ASR), which is a similar expansion phenomenon, and thus, it is possible that when expansion

---

[*1] Ph.D (engineering), Professor, Civil and Environmental Engineering, Department of Systems Innovation Engineering, Faculty of Engineering, Iwate University (fellow)

[*2] Dr. Eng., Senior Researcher, National Institute of Maritime, Port and Aviation Technology, Port and Airport Research Institute (full member)

[*3] Dr. Eng, Solution Sales Dep., Taiheiyo Consultant Co., Ltd. (full member)

[*4] Dr. Eng., Research Scientist, Central Research Laboratory, Taiheiyo Cement Corporation, (full member)

[*5] Dr. Eng., Assistant Manager, Materials Laboratory, Materials Department, Testing and Research Center, General Building Research Corporation of Japan (full member)

occurs due to DEF, it may negatively affect structural performance, causing cracks and excessive deformation. However, presently, findings on DEF have not been organized systematically, and in Japan, the risk of expansion due to DEF and the resulting deterioration in structures (DEF-related deterioration) remains unclear. On the other hand, in the "Guidelines for Control of Cracking of Mass Concrete" (hereinafter, the Mass Concrete Guidelines)5) of the JCI, the verification of DEF cracking has been added, so it is possible that actual cases requiring preventive measures for DEF will increase in future.

Against such a background, the JCI-TC173A "Technical Committee on Delayed Ettringite Formation" was established to organize the latest information on DEF and re-discuss the risk of deterioration in structures due to DEF. Over a 2-year activity period, four working groups (WGs) were organized to discuss four points: mechanisms of expansion due to DEF, diagnosis based on material science, comparison of real cases between overseas structures and structures in Japan, and preventive measures for structures. Based on these findings, current problematic issues and future research needs were discussed, from a wide range of viewpoints. In this paper, a summary of the results of this activity and the future scope for DEF research are reported. **Table 1** shows the technical committee membership.

Table 1: Technical committee membership

Chairman	Shunsuke Hanehara	Iwate University
Chief Secretary	Yuichiro Kawabata	Port and Airport Research Institute
Secretaries	Shoichi Ogawa	Taiheiyo Consultant
	Hikotsugu Hyodo	Taiheiyo Cement Corporation
	Natsuki Yoshida	General Building Research Corporation of Japan
Members	Shingo Asamoto	Saitama University
	Yosuke Higashi	Oriental Shiraishi Corporation
	Go Igarashi	Tohoku University
	Motoki Uehara	Railway Technical Research Institute
	Tatsuya Usui	Taisei Corporation
	Isao Kurashige	Central Research institute of Electric Power Industry
	Suguru Saito	Niigata University
	Koji Tamataki	Ube Industries, Ltd.
	Atsushi Teramoto	Hiroshima University
	Takeshi Torichigai	Kajima Corporation
	Tetsuro Matsushita	Takenaka Corporation
	Hiroshi Nomura	Sumitomo Osaka Cement Co., Ltd.
	Shintaro Miyamoto	Tohoku University
	Shiro Muraoka	Central Nippon Expressway Co., Ltd.
	Taiichiro Mori	Denka Company Limited
Advisor	Yoshikazu Sato	Hiroshima University
Former member	Yukiko Nishioka	Takenaka Corporation

2. Potential of DEF-related expansion in concrete and risk of DEF-related deterioration in structures

The term DEF indicates delayed formation of ettringite (Ett). DEF itself is sometimes thought to lead to deterioration in the form of cracking and excessive deformation in structures, but this is not always true. Consequently, this technical committee first clearly divided DEF into delayed formation of Ett and the resulting expansion, based on the results of chemical reactions.

Subsequently, we classified the potential by which concrete undergoes DEF-related expansion, and the possibility that structures is affected by DEF-related deterioration in the concrete. In other words, the former involves the DEF-related expansion potential of concrete, and the latter involves the risk of DEF-related deterioration in structures **(Figure 1**). Furthermore, DEF-related deterioration encompasses deterioration in structures due to DEF-related expansion, for example, deformation, cracking, and decreased load-bearing capacity. DEF-related expansion potential in concrete is affected by the high-temperature action and material composition.

On the other hand, discussions on the risk of DEF-related deterioration in structures should include DEF-related expansion potential and the specific construction type, form, dimensions, and exposed conditions of structures. Furthermore, such discussions must be in terms of the movement of moisture and mass transfer, and constraint conditions. At the present research level, it is quite difficult to quantitatively discuss the risk of DEF-related deterioration in structures, but, in discussing how to address the risk of DEF-related deterioration in structures, the potential and risk are often confusing; therefore, this technical committee has clearly divided them. The approaches we have taken are mainly from the viewpoint of DEF-related expansion potential (Chapters 3 and 4) and the risk of DEF-related deterioration (Chapter 5).

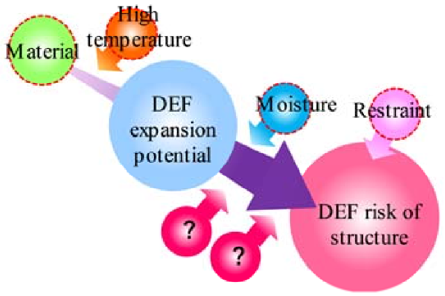

Fig. 1: Conceptual diagram of DEF-related expansion potential and DEF-related deterioration risk (red dotted line circles are factors corresponding to risk)

2.1 DEF-related expansion potential of concrete

The DEF-related expansion potential of high-temperature cured concrete is affected not only by high-temperature action, but also by multiple factors including the materials used in concrete and the mixture thereof (please See Chapter 3 for details). In general, based on the fact that cement in Japan has a lower SO_3 content than cement overseas (**Figure 2**), it has been recognized that the DEF-related expansion potential of concrete is low. However, based on the results of recent laboratory tests, cement and concrete reportedly undergo DEF-related expansion if they have a constant or higher high-temperature history (80 °C or higher without SO_3 addition in data for Japan)$^{6)}$. Considering the fact that there are many structures in Japan that experience high-temperature action exceeding 70 to 80 °C (Chapter 5), it is a valid assumption that concrete possesses DEF-related expansion potential if it experiences high-temperature action.

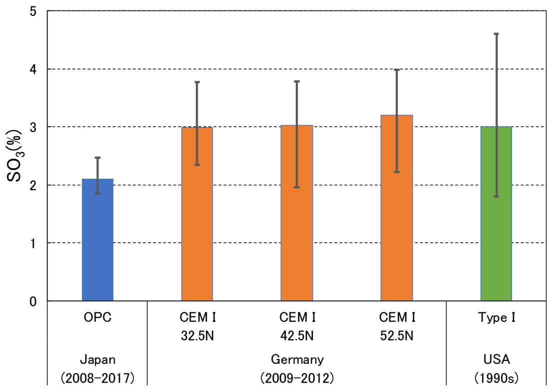

Fig. 2: Comparison of the amount of SO_3 in each cement in each country

2.2 Risk of DEF-related deterioration in structures in Japan and warnings from overseas work

In Japan, there are several structures for which the possibility of DEF-related deterioration has been indicated$^{3),4)}$. Presently, there have been no reports of cases in which such deterioration has clearly occurred in structures. In this technical committee, we investigated the risk of DEF-related deterioration in structures, compared to published information$^{2)}$ on structures with DEF-related deterioration in France (Chapter 5). Based on the results, although the comparison was made with limited information, no major differences were found between the characteristics of structures with DEF-related deterioration in Japan and France. In other words, although these were not considered to be the main factors behind DEF-related deterioration, the possibility of other factors and of being strongly influenced by the combined action of various factors, was considered.

In overseas work, the risk of DEF-related deterioration is often unclear because of the use of local materials. In particular, cases of suspected DEF have been reported in Asia5), but sometimes, temperature control has already been outlined based on BS and ACI in overseas work. Nevertheless, due to the particularly low level of experience found in overseas construction work, it is essential that attention be paid to DEF-related deterioration.

2.3 Differences between potential and risk

As described above, most concrete structures may have the potential for DEF-related expansion. However, presently, there are very few reports of structural deterioration and damage due to DEF in Japan. This suggests the possibility that even if the DEF potential of concrete is high, the risk to a structure may be lower than assumed. In other words, DEF potential and risk of DEF-related deterioration are not equivalent. Thus, there is a need for future research that considers how to address the risk of DEF-related deterioration in structures, clarifies the effects of other factors, and links the expansion potential to the deterioration risk.

For example, the mass of concrete at a particular temperature is generally concentrated at the center of members, and thus, these areas have the highest expansion potential. On one hand, the present understanding of the DEF mechanism is that reduced alkalinity of pore solution is required for DEF-related expansion, thus it is not clear whether risk at the center is necessarily high in terms of moisture supply and mass transfer. Presently, cases of DEF-related deterioration in Japan are quite limited, and although still largely based on assumptions, it is essential to consider ways to address the risk of DEF-related deterioration. Furthermore, it is important to not only discuss DEF-related expansion potential, but also identify its complex relationships with other factors.

2.4 Addressing the risk of DEF-related deterioration and scope of future research

In general, the ways of addressing risk may be broadly divided according the possibility of risk and its consequences. It is quite difficult to quantitatively evaluate the possibility of risk arising and the degree of consequence for DEF-related deterioration. Therefore, to reliably control DEF-related deterioration, its prevention is required in the Mass Concrete Guidelines5). The locations to be verified are determined based on the moisture supply, and then concrete is checked for deterioration by determining the limit value of the maximum temperature corresponding to the concrete material composition and mixture. The IFSTTAR DEF-related deterioration prevention Recommendation$^{2)}$ is another approach similar to the Mass Concrete Guidelines. However, it is somewhat different, in that moisture supply is divided into several levels, and in addition to considering the importance of structures, the level of precautions is determined from risk matrices.

Presently, there are several unknown aspects of DEF-related deterioration, so minimization of DEF-related expansion potential is the main method for addressing risk. This necessitates preventive measures regarding concrete material composition, and mixing, or construction (max temperature). The demand for absolutely zero expansion potential in Japan is understandable since the risk of DEF-related degradation remains unknown. However, methods combining several influencing factors in a complex manner to reduce deterioration risk by degrees need to be developed. Thus, systematic research is essential.

In addition, extensive research into the consequences of DEF-related expansion on the structural performance of structures or members is needed. The DEF expansion rate is considerable, and relatively large compared to ASR, so there is a high possibility of decreased structural performance. However, presently, there are very few studies at the member level, either within or outside Japan. There are reports that, according to laboratory experiments, the deformation behavior of RC beams due to DEF-related expansion differs significantly from that due to ASR expansion. On the other hand, there are reportedly results from greatly reducing the expansion rate by using steel material restraints, although there are areas in which it is unclear how structures deteriorate from DEF-related expansion. For example, in the case of ASR, preventive measures are taken, such as restricting the total alkali content during construction. It is recognized that this provides consistent risk reduction; if ASR does occur, corrective maintenance (Category B operation and maintenance per written statement of the Japan Society of Civil Engineers) is performed. In the case of ASR, there are structures with previous deterioration, for which corresponding repair techniques have been established. Therefore, several corrective maintenances are possible. As stated above, even if we assume DEF-related free expansion to be much larger than ASR expansion, if restrained DEF-related expansion is approximately the same as ASR, then there is a reasonable possibility that it may be controled at the operation and maintenance stage. Thus, there is no need for protective measures during design, although the idea of reducing risk in both design and operation and maintenance should not be excluded, and there is a need for further ongoing discussion. To that end, not only material, but also structural research is essential.

Furthermore, there need to be systematic discussions on inspection techniques and protective measures for accomplishing design and inspection at the required level, as DEF-related deterioration measures, as well as operation and maintenance techniques to address any possible DEF. In addition, protective measures inevitably incur costs during construction, and there needs to be active multifaceted research to ensure reasonable accountability.

3. Mechanisms of DEF-related expansion

DEF is a phenomenon that occurs in hardened cement bodies with a history of high temperatures at the initial material age. Ettringite that had been decomposed is subsequently formed, and then, depending on the circumstances, expansion occurs. However, there is no direct correlation between the amount of ettringite formed and the expansion. Ettringite is observed even in concrete with no deterioration, and macroscopic ettringite does not contribute to expansion with DEF. Such phenomena make it difficult to understand the mechanism of DEF. The mechanism of DEF-related expansion is not fully understood, and there remain many conflicting opinions and questions. **Table 2** shows the mechanism of DEF deterioration, together with the related main reactions, according

Table 2 DEF-related deterioration propagation mechanism and main reactions

Propagation stage	Main reaction	Notes
Mix forming (pre-curing period)	・Ettringite outgrowth	・Ettringite formation as small crystals in sections with a dense mixture of inner products and outer C-S-H
High-temperature curing	・Ettringite decomposes, and sulfate ions and aluminate ions are released into the pore solution ・Inner C-S-H forms, and takes in sulfate ions and aluminate ions	・At the higher temperature, ettringite decomposes more easily ・Sulfate ions are adsorbed by the inner C-S-H surface, and adsorption increases at high pH, high temperatures, and high ion strength. ・Aluminate ions are taken into the inner C-S-H structure ・It is thought that sulfate ions and aluminate ions taken into the inner products might not be come from only decomposed ettringite ・It is thought that ettringite that has been decomposed exists as a fine monosulfate in places where ettringite was formed. ・The timing of ettringite decomposition and inner C-S-H formation adsorbing sulfate ions are important factors that determine whether suitable pre-curing periods and suitable curing temperature periods are needed to generate the most expansion
Room-temperature curing (wet environment)	・Temperature, pH, and ion strength decrease → Sulfate ions and aluminate ions are released from the inner hydrate → Ettringite forms easily (solubility decreases) ・Ettringite crystals form, and expansion pressure is generated in microscopic areas with a dense mixture of inner products and outer C-S-H ・Fine-scaled ettringite reprecipitates in cracking and coarse pores through Ostwald ripening	・Adsorption of sulfate ions into inner C-S-H is completely reversible, and sulfate ions are released depending on pH, temperature, and ion strength, and are supplied to the outer products on a concentration gradient ・Ettringite formation in a microscopic area is regarded that monosulfates as crystal nuclei, and aluminate ions are supplied from the inner C-S-H ・Ettringite crystals forms in finer pores exhibit a larger expansion pressure ・Aggregate does not expand with DEF; therefore, gaps are formed at the interface of aggregate and expanded paste sections. Ettringite crystals form in gaps due to Ostwald ripening. They do not contribute to expansion (paste expansion hypothesis). However, it is also believed that ettringite generated in gaps also contributes to expansion (crystal growth pressure hypothesis).

<Terms>

Inner products: Hydrates forming in places where cement particles were present.

Inner C-S-H: C-S-H generated as the inner products. Even with inner C-S-H, at the stage immediately after high-temperature curing, electron density is high, and the C-S-H appears bright under an electron microscope, and thus is also referred to as lighter C-S-H. In addition, when the hydration proceeds, the density decreases, and sections that appear dark are generated, so these are also referred to as darker C-S-H.

Outer products: Hydrates forming on the outside of sections where cement particles are present (place where mixed water existed).

Outer C-S-H: C-S-H generated as the outer hydrate is referred to as the outer C-S-H.

to current understandings. Expansion due to DEF is considered as a chemical reaction, but there are major physical factors contributing to mass-transfer resistance. Below, expansion due to DEF and the material science findings based on this table.

3.1 Ettringite and its stability

Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) is a columnar mineral with a hexagonal cross-section often having crystallization water even within hydrates of cement materials. It sometimes grows in the cement paste to a length of over several microns. The stability of ettringite is affected by ambient temperature and liquid-phase pH. Ettringite exists stably at lower temperatures below 60–70 °C, and monosulfate (Ms) at higher temperatures. Ettringite generated prior to a history of high temperatures decomposed during high-temperature curing. The constituent sulfate ions and aluminate ions are released through pore solution, and taken up by the inner calcium-silicate-hydrate (C-S-H).

3.2 Role of C-S-H in DEF

(1) Role of ion supply sources

Figure 3 shows the inner C-S-H immediately after high-temperature curing (C-S-H generated inside cement particles), and the composition of the inner C-S-H after water curing, moist-air curing, and KOH-solution curing at the same concentration as a pore solution, for 200 days after high-temperature curing7). Sulfur (S) and aluminum (Al) are present in high concentrations in the inner C-S-H formed immediately after high-temperature curing (black circles ● in figure), which is due to the sulfate ions (generated by ettringite decomposition during high-temperature curing) being adsorbed into the inner C-S-H, and aluminum ions being taken into the C-S-H structure. In addition, with water curing at room temperature for 200 days, the concentrations of S and Al in the inner C-S-H (black triangles ▲ in figures) decrease, so the ions are released from the inner C-S-H to form ettringite. When a KOH solution in room-temperature curing with the same concentration as the pore solution is used, there is a small decrease in S concentration (grey □ in figure), and expansion is delayed. These show that if alkali is leached to the outside in a wet environment after high-temperature curing, S and Al are supplied to pore solution from the inner C-S-H, producing ettringite.

Furthermore, completely reversible adsorption of sulfate ions into C-S-H occurs on the surface of C-S-H, and increases further with high pH, high temperatures, and high ion strengths8). In addition, adsorbed sulfate ions are thought to be released into the pore solution from the inner C-S-H by a concentration gradient during periods of cooling from high-temperature curing, and subsequent room temperature curing.

(2) Ettringite formation at the microscopic scale

Figure 4 shows a conceptual diagram of the mechanism of DEF-related expansion, as presented by Taylor, et al.9). Ettringite formed during curing at room temperature prior to high-temperature curing is produced by the reaction of the calcium aluminate phase (C_3A) and gypsum, and is occurs as a small crystal finely mixed with outer C-S-H. This ettringite is decomposed to form monosulfate by high-temperature curing, as shown in the top half of **Figure 4**. When ettringite is decomposed, sulfate ions and aluminate ions are taken into the inner C-S-H.

In subsequent wet environments, alkali is leached from the system, resulting in reduced pH and ion strength; and sulfate ions are desorbed from the inner C-S-H and released into the pore solution. The temperature also decreases, so the solubility of ettringite decreases, which facilitates precipitation. Ettringite is, thus, generated within microstructures created by the outer C-S-H, and expansive pressure is exerted. This stage is as shown in the bottom half of **Figure 4**. Ettringite in microstructures is about 5 μm or less in size, and this fine ettringite generation is responsible for producing large expansion. Furthermore, the crystallization pressure is known to depend on pore shape and supersaturation. According to Scherer, et al.10), when the curvature of the crystal/solution interface in pores is κ_{CL}, and the surface energy is γ_{CL}, equation (1) can be led. Crystallization pressure is inversely proportional to the size of the pores thus grown, and a large crystal growth pressure is exhibited. This idea has been applied to DEF-related expansion 11).

$$\gamma_{CL}\kappa_{CL} = \frac{RT}{v_c} ln\left(\frac{Q}{K}\right) \qquad (1)$$

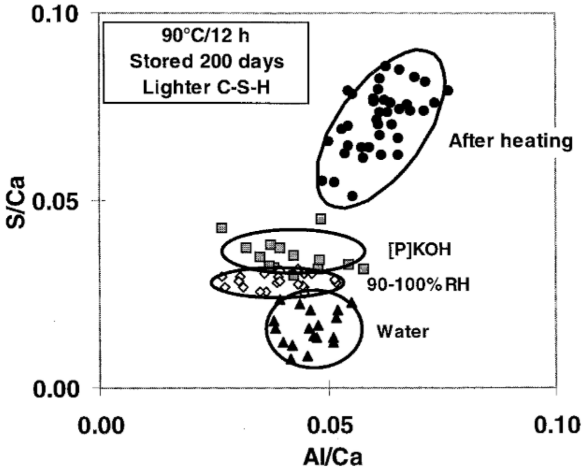

Fig. 3: S/Ca ratio and Al/Ca ratio of the inner C-S-H of (water and KOH solution) with 200-days room temperature curing after 90 °C curing[7)]

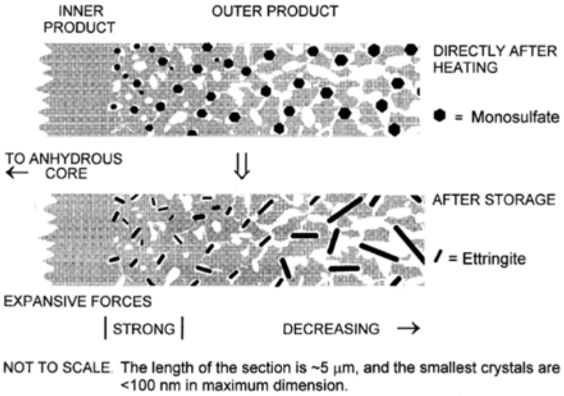

Fig. 4: Conceptual diagram of the mechanism of DEF-related expansion[9)]
(Shared areas are solid phase; white areas are pores)

3.3 DEF and ASR

The visual appearance related to deterioration of DEF is quite similar to that of ASR. In addition, in terms of the chemistry, there is no method to control chemical reactions. However, if microcracking occurs with expansion and then water is supplied, it may be possible that another reaction can be accelerated. The mechanism of combined DEF and ASR has been experimentally investigated in Japan[12)], for example, but it is not yet fully understood. Many issues remain with regard to diagnostic methods that may be used to identify the causes of deterioration and make future predictions.

3.4 The factors behind DEF-related expansion

(1) Cement composition, etc.

There have been several findings on the factors affecting DEF-related expansion. These findings focus on the amount of SO_3 in a system and the SO_3/Al_2O_3 ratio. In general, the larger the SO_3/Al_2O_3 ratio, the greater the alkali content (Na_2O_{eq}) and the larger the specific surface area, and the more likely it is that expansion due to DEF will occur. In addition, reportedly, the SO_3 content at which expansion due to DEF is largest as a result of alkali content, changes; in other words, the pessimum phenomenon can possibly occur. It is difficult to predict expansion due to DEF perfectly using this index. A predictive formula was also proposed, which is called as a DEF index, taking type and content of cement minerals, and alkali content (Na_2O_{eq}) into account13,14).

(2) Pre-curing period, high-temperature curing temperature and period

There are cases in which DEF-related expansion has been studied in terms of its relationship with the pre-curing period, high-temperature curing temperature, and period under various conditions. These factors are not independent. There are ranges and threshold values at which expansion is likely to occur due to the complex interactions between the SO_3 content, alkali content, and other minerals. In general, about four hours of precuring is the most severe for DEF expansion. The threshold value of high-temperature curing temperature at which expansion occurs is thought to be between 60 and 70 °C. It is thought that the timing of ettringite decomposition and the formation of inner C-S-H is important from a mechanism viewpoint. In addition, high-temperature action does not occur only during the initial period. It is reported that DEF-related expansion occurs even when concrete is exposed to high temperature after hardening15).

(3) Supplementary cementitious materials (SCMs)

There have been several significant findings regarding the effectiveness of SCMs to mitigate/inhibit DEF expansion, but few findings on mechanisms. The amount of fly ash, ground granulated blast-furnace slag, metakaolin and other mixing materials generally mitigate DEF-related expansion, but silica fumes have relatively little effect16). SCMs often contain Al, and reducing the SO_3/Al_2O_3 ratio and replacement of SCMs tends to be inhibitive. However, in some cases, depending on the replacement level, the effectiveness is negative, and also, the latency time is inversely shorten. As for the SCMs that demonstrate mitigating effects, although ettringite is formed when the Al content rate is high, no expansion is demonstrated16), and there remain many questions from a mechanism viewpoint. In addition, it has been pointed out that densification due to hydration of SCMs reduces permeability and controls DEF-related expansion17).

(4) Aggregate

Expansion due to DEF also occurs in cement paste, so the presence of aggregate is not essential.

However, the presence of aggregate and increased particle size increases the expansion rate. It is found that the presence of interfacial transition zones accelerate alkali leaching, whereby the mass transfer resistance of the sulfate ions required for ettringite formation, decreases. In addition, it has been indicated that expansion is promoted depending on the type of aggregate used, and with DEF, the thermal expansion coefficient of aggregate has an influence as the high-temperature curing process proceeds18). In the case of limestone aggregate, a part reacts with cement in addition, to the above effects, which generates carboaluminates. This improves the quality of the transition zones, so it is thought that the presence of aggregate has the effect of increasing the latency time of expansion. On the other hand, cases in which limestone aggregate has been observed to a negative effect on DEF-related expansion1) have been reported, and additional research is required.

3.5 Constraints on DEF-related expansion

There has been little research on the influence of constraints on DEF-related expansion, but the properties of cracking in RC structures due to DEF are known to be strongly influenced by constraints. With ASR, in which internal expansion occurs similar to DEF, ASR gel, which is the driving force of expansion, is visco-elastic, so the expansion pressure in the constraint direction is mitigated by the movement of ASR gel, and expansion perpendicular to the constraint becomes larger. On the other hand, it is found that with DEF, neither constraints nor a prestress has a significant effect in directions without applied stress, as constraints and prestress reduce only DEF-related expansion in the constraint direction19).

4. Literature review on diagnosis of DEF and cooperative test

4.1 Literature review on diagnosis of DEF

(1) Microscopy

In diagnosis of DEF, microscopic observation of concrete is of great importance. Hime, et al. indicate the importance of distinguishing DEF from ASR when observing samples with a stereoscopic microscope, polarizing microscope or scanning electron microscope (SEM)20). Johansen, et al. state that ASR is characterized by cracking occurring in aggregate particles and extension of the cracks into the surrounding cement paste. On the other hand, expansion of paste due to ettringite formation is characterized by observing “gaps” around the aggregate21). Hime, et al.20) and Thomas, et al.22) both similarly claimed that attention should be paid to gaps around the aggregate for DEF diagnosis. However, a caution is that if DEF-related expansion occurs in actual concrete structures under constraint, then, in some cases, no clear gaps are seen.

In addition, Famy investigated the paste experiencing a history of high temperatures, and reported that so-called inner C-S-H generated at high temperature becomes dense. Compositional images becomes lighter (lighter C-S-H), and for inner C-S-H generated inside of the lighter C-S-H during after-curing, compositional images appear relatively dark (darker C-S-H)7). It is reported that the generation of lighter/darker C-S-H should be focused on in the microscopic observation for the purpose of determining whether there is a high-temperature history or not.

(2) Instrumental analysis

XRD is not considered very useful for DEF diagnosis20) due to its inability to analyze ettringite with low crystallinity20) and the fact that no correlation is found between the amount of ettringite formed and expansion due to DEF23). On the other hand, SEM-EDS is used for composition analysis of inner/outer C-S-H in laboratory experiments (investigation described in 3.2 (1), etc.), and it is expected for it to be applied to DEF diagnosis.

(3) Core expansion test

LCPC (presently IFSTTAR) in France proposed core expansion test for DEF (LPC Test Method No. 67)24). The optimum collection position is determined, and a core 80–110 mm in diameter (150 mm in the case of a dam) and 150–200 mm in length is collected. After immersing it for one day in water at 20±2 °C, a gauge plug is attached to a side of the test core. Thereafter, the test core is again immersed in water, and changes in length are recorded for at least one year. After testing, it is recommended that the condition of the deterioration should be observed by SEM.

In addition, Thomas, et al. proposed a core expansion test, which was applied to several bridges affected by DEF22). φ50 mm × 100 mm core samples are taken from real structures, and then immersed in a $Ca(OH)_2$ solution (room temperature) and 1 M NaOH solution (80 °C). If the core expands in the former, DEF is thought to be the cause of deterioration. If it expands in the latter, ASR is thought to be the cause.

4.2 Literature review on predictive methods for DEF expansion

(1) Predicting the potential of DEF using analytical values of cement

Zhang et al. used analytical values of cement, and found that when SO_3/Al_2O_3 is 0.8 or higher and the DEF index $[(SO_3/Al_2O_3)\times((SO_3+C_3A)/10)\times(Na_2Oeq)^{1/2}]$ is 1.1 or higher, DEF expansion occurs[13)]. However, it has been pointed out that this index may not accurately predict DEF[6)].

(2) Concrete expansion test

LCPC proposed a method for testing expansion of concrete specimens (LPC Test Method No. 66)[25)]. After subjecting test pieces using real mixtures in simulated real environments to two cycles of high-temperature curing for seven days in water at 20 °C and seven days at 38 °C with an RH of 30%, they are immersed for at least 12 days in water at 20 °C. DEF potential is determined according to standards indicated in the 2017 revision of IFSTTAR guidelines (2018 English version)[2)].

4.3 Actual cases of DEF diagnosis

According to past reports, there have been various cases of DEF diagnosis. These include steam-cured sleepers, mass concrete, ASR diagnosed as the primary factor, DEF promoting ASR, and ASR promoting DEF.

The details of these are assembled in the final report of this technical committee. In all of these cases, diagnosis was done mainly using microscopy. In addition, in ASR-combined cases, the presence of ASR and DEF was determined using ASR diagnosis, for which detailed techniques had been established (petrographic investigations, core expansion test, etc.). In DEF diagnosis, distinguishing DEF from ASR is an important point. Furthermore, there are also cases in which checking DEF against recently reported mechanisms does not necessarily produce accurate diagnosis; thus, caution is required.

4.4 Cooperative test on test pieces deteriorated by DEF-related expansion

(1) Purpose of cooperative test

Cooperative test was conducted for the purpose of having the same test pieces analyzed by the members of a diagnosis SWG, tracing existing findings to obtain a clearer understanding of phenomena and establishing common recognition and subjects. In this paper, we report some of the results.

(2) Summary of test pieces

Silica sand and white Portland cement were used. **Table 3** lists the chemical components of cement. 40 mm × 40 mm × 160 mm test pieces were manufactured with W/C = 50% and S/C = 1.0 mortar, and after four hours of pre-curing at 20 °C, high-temperature curing was performed for 10 hours at

90 °C. After being allowed to cool, the pieces were left to stand for 11 years in 20 °C water, and then used as test samples. The final expansion after 11 years was approximately 2%. Photo 1 shows the appearance of the test sample.

Table 3: Chemical components of cement

Chemical components (%)							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
22.88	4.60	0.19	65.13	1.35	2.52	0.05	0.06

Photo 1 Appearance of test piece

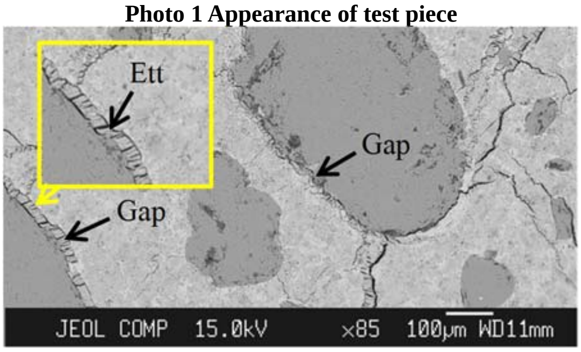

Photo 2 Gaps and ettringite around aggregate

(3) Summary of test results

SO_3/Al_2O_3 calculated from cement composition was 0.698, and the DEF index was 0.3. Regardless of the fact that these values were less than the threshold reported in the literatures, the mortar expanded by approximately 2%. It was found that it was not possible to accurately predict DEF with the predictive index that were used.

Photo 2 shows the results of observing test pieces using SEM. Gaps formed around aggregates, and gaps and cracks in paste were mostly filled with ettringite. It was possible to clearly observe the characteristics of DEF available in literature$^{20-22)}$. An analysis of the paste was attempted through elemental analysis with wavelength-dispersive X-ray spectroscopy (WDS), but submicron-scaled ettringite in the paste were presumably dissolved to form macroscopic ettringite in gaps and cracks during long-term immersion; thus, fine-scaled ettringite could not be found in the paste. Similarly, observation of inner C-S-H in cement particles was attempted, but it was difficult to distinguish between lighter CSH and darker CSH, probably because of considerable hydration over 11 years. Furthermore, no signs of ASR were found in the sample.

(4) Summary of cooperative test

As shown in the past studies[20–22], gaps were found around the aggregate. These characteristics may be useful to be identified for DEF diagnosis.

As indicated in existing literature[20], it is important to distinguish DEF from ASR for diagnosis of DEF. In the cooperative test here, this could not be studied. Questions remain about the interaction of DEF and ASR; thus, further research is needed.

5. Risk of DEF-related deterioration in structures and members

The actual temperature history and material composition, as well as member dimensions, of massive concrete structures and precast members in Japan were surveyed based on DEF occurrence factors such as max temperature limit values and the type and composition of materials, shown in guidelines for DEF[2),5),26] in Japan and abroad.

5.1 Massive concrete structures

Table 4 summarizes existing literature in Japan (239 cases) and organizes information on structures (37 cases) with maximum internal temperatures of concrete members exceeding 60 °C, according to actual measurements or numerical analysis. Bridge superstructures with a history of high temperature were mainly cases involving concrete containing 400 kg/m^3 or more of high-early-strength Portland cement. In addition, cases have been confirmed of high temperatures being reached during winter periods, through heated or insulated curing. There were several cases of bridge substructures using Portland blast-furnace slag cement (type-B) or low-heat Portland cement, and the cement content also tended to be small compared to that of bridge superstructures. However, cases were confirmed of summer construction or thick members in which temperatures reached 80 °C or more despite using pipe cooling. There were also cases in which consecutive underground walls reached temperatures of 85 °C or higher.

Table 4: Examples of domestic mass concrete structures

Item	Bridge		Ordinary structure	Hydraulic structure
	Superstructure	Substructure		
Number of data	10	13	12	2
Max temperature (°C)	65–86	63–83	60–87	61–64
W/C (%)	35–42	34–55	42–60	43–55
Cement content (kg/m^3)	393–472	280-473	269–418	269–358
Cement type	H, N, BB	BB, N, L, H, M	BB, N, L	BB, FB
Member thickness (m)	0.5–5.8	1.0–8.5	0.8–4.5	2.0–3.0

5.2 Precast members

Precast members are also investigated, considering recommended values for curing temperature and the temperature history of actual members. According to a summary of curing temperatures for precast members shown in several standards[27)-29)], steam curing temperatures of 65 to 70 °C or less were recommended. According to an investigation, based on recommended values in standards and curing fuel costs, steam curing temperatures in product plants often seemed to be within a range of about 40 to 60 °C. On the other hand, internal temperatures of the member are known to not necessarily match curing temperatures, owing to the heat of hydration of cement. According to an investigation on precast PC girders (member thickness: 0.7 m), sometimes, the maximum internal temperature of members reaches 80 °C or more even if the steam curing temperature is maintained at 50 °C. In addition, ordinary and high-early-strength Portland cement, which have a relatively fast hydration reaction, were often used in precast members.

5.3 Risk of DEF-related deterioration

Based on the results of checking the occurrence conditions of DEF-related deterioration shown in guidelines in Japan and abroad against massive concrete structures and precast members in Japan, and comparisons of the characteristics of structures and members that may be at risk of DEF-related deterioration, there were several structures in Japan which could not be verified by the guidelines. In addition, it was confirmed that there were many presented cases similar in characteristics to those of DEF-related deterioration structures in France (**Table 5**)[30)]. Owing to lower SO_3 and C_3A contents in CEM I (Portland cement) in Japan than other countries (**Table 6**), it is possible that this difference in composition has a strong influence on the real cases.

However, in the Bridge 2 example, DEF-related deterioration occurs in compositions similar to those of cement in Japan. In addition, there are also examples of CEM II/A (20% mixing materials or less).

When comparing these only in terms of their numerical values and consider the range of chemical compositions of cement in structures in Japan alone, there is nothing strange about DEF-related deterioration occurring in them. On the other hand, while extreme DEF-related deterioration in which cracking on the order of several mm reportedly occurs in foreign structures under similar conditions, no major cases have been reported in Japan. Moreover, presently the causes of DEF-related deterioration cannot be clearly explained with these factors alone. Thus, there will be a missing link between the potential and the risk of DEF expansion that have presently been presented. As stated in Chapter 2, future research is essential.

Table 5: Characteristics of structures with DEF-related deterioration in France[30)]

	Bridge 1	Bridge 2	Bridge 3	Bridge 4	Bridge 5	Bridge 6
Date of construction	1955	1990	1980	1988	1982	1989
Structural part	Cap beam	Base of pylon	Cap beam	Pier	Cap beam	Base of pier
Delay in occurrence of damage (years)	27	6	9	10	10	8
Environment	Water proofing Problem	Immersed & variable immersion	Lack of drainage	Immersed & variable immersion	Exposure to rains	Rains and capillarity
Maximum temperature (°C)	80	79	80	80	69	75
W/C	0.5	0.5	0.5	0.5	0.5	0.5
Cement type	CEM I	CEM I	CEM I	CEM II/A	CEM I	CEM II/A
Cement content (kg/m^3)	430	400	400	380	350	385
SO_3 content (%)	2.5	2.8	2.6	2.5	3.4	2.5
C_3A content (%)	11.2	8.2	9.8	7.0	10.4	7.0

Table 6: C_3A and SO_3 contents of Portland cement in Japan[31)]

Type of cement	C_3A (%)	SO_3 (%)
Ordinary	9.07	2.10
High-early-strength	8.41	2.98
Moderate heat	3.48	2.24
Low heat	2.51	2.38

6. Comparison of protective measures between foreign and domestic guidelines

6.1 Comparison of temperature regulation values between foreign and domestic guidelines

The regulations related to temperature history in foreign and Japanese guidelines were summarized, and the preventive measures for DEF were compared. In foreign guidelines, 65 to 70 °C has been adopted as the limit value for temperatures related to DEF-related deterioration, and a maximum of 85 °C is allowed depending on differences in material (especially the type of cement and the replacement level of SCM). The Mass Concrete Guidelines similarly adopts 65 to 80 °C depending on the cement type and replacement level of SCMs.

6.2 Operational and technical issues facing the Mass Concrete Guidelines

The workflow for verification of DEF cracking in the Mass Concrete Guideline from the viewpoint of designers and contractors was investigated. In addition, decision-making methods for max temperature limit values in the Mass Concrete Guidelines was investigated. In the Mass Concrete

Guidelines, decisions are made based on the total SO_3 content or total alkali content in concrete. Based on mechanisms, the possibility of DEF expansion is mainly decided by the balance of SO_3 content and Al_2O_3 content, and it also may be reasonable to decide temperature regulation values based on the basis of the weight of cement. Regulation values in the Mass Concrete Guidelines are set after converting mortar and concrete data into 300 kg/m^3 unit cement content. For example, 9 kg/m^3 total SO_3 content means that the SO_3 content of cement is 3% with 300 kg/m^3 unit cement content, but if 500 kg/m^3 concrete is manufactured with the same cement, the total SO_3 content is 15 kg/m^3. In extreme terms, the larger the unit cement content in cement paste, the higher the risk of DEF.

In terms of total alkali content, Japanese cement is generally low alkali-type cement (equivalent alkali content 0.5 to 0.6%), and it does not exceed 3.0 kg/m^3 in ordinary mixtures. Although concrete exceeding a total alkali content of 3.0 kg/m^3 may still be used for ultra-high-strength concrete, for example, no experiments on ultra-high-strength concrete have been conducted with original data, so it is possible that the applicable range may be exceeded. Although it is possible that these regulation values may be exceeded in concrete by adding accelerating agents or other additives, doubt remains as to whether the assumed temperature range in the Mass Concrete Guidelines is reached. The total alkali content in concrete of 3.0 kg/m^3 or less is also very important from the viewpoint of ASR, and when considering the possibility that ASR promotes DEF, there is a need to take another look at regulation values for total alkali content.

In addition, when considering previous experimental facts, increased cement content does not necessarily lead to increased DEF risk. It is generally understood that decreased W/C inhibits mass transfer and delays DEF-related expansion. For example, according to the Mass Concrete Guidelines, PC structures with low W/C represent a high risk of DEF-related deterioration. On the other hand, PC structures are high in mass transfer resistance and do not allow cracking, so it is believed that DEF may not occur over long periods. However, if one looks at the effects of delaying latency time, there is still much to discuss. There needs to be further verification of the validity of regulating temperature by total alkali or total SO_3 content.

This technical committee did not reach the point of offering specific guides for solving the above problems. However, we organized items that should be discussed regarding the handling of DEF in the Mass Concrete Guidelines in future.

7. Conclusion

This technical committee addressed DEF-related deterioration in structures from a wide range of viewpoints ranging between material science mechanisms and analysis real structures. In conclusion, the current understanding is that it is difficult to quantitatively identify the risk of DEF-related deterioration in Japan, but this technical committee has taken a bottom-up approach to understanding DEF, and has presented subjects and issues for future research. In particular, DEF research is insufficient from the perspective of the structural field, and what happens to structures with extreme expansion due to DEF is still not fully understood, which will be a major research issue. For the future, the committee hopes that there will be more extensive studies on DEF in order to adequately reduce the risk of DEF-related deterioration, from the design of concrete structures to their construction, operation, and maintenance, based on the findings of this technical committee.

References

1) Yuichiro Kawabata, Hiromichi Matsushita: A study of DEF-related expansion in concrete subjected to high-temperature steam curing, Journal of JSCE E2, Vol. 67, No. 4, pp.549-563, 2011
2) IFSTTAR: Recommendations for preventing disorders due to delayed ettringite formation, 2018
3) Koji Tsuruta, et al.: Study of delayed ettringite formation in cast-in-place concrete structures, Proceedings of the Japan Concrete Institute, Vol. 37, pp.679-684, 2015
4) Kazuhiko Goto, Shoichi Ogawa, Naotsugu Higashimaru: Case study of abutment with suspected deterioration due to delayed ettringite formation (DEF), Japan Society of Civil Engineers 73rd Annual Meeting, pp.783-784, 2018
5) Japan Concrete Institute: 2016 Guidelines for Control of Cracking of Mass Concrete, 2016
6) Yuichiro Kawabata, et al.: Evaluating factors influencing DEF-related expansion based upon long-term laboratory testing, Cement Science & Concrete Technology, Vol. 69, No. 1, pp.527-534, 2015
7) Famy, C., Scrivener, K.L., Atkinson, A., Brough, A.R.: Influence of the storage conditions on the dimensional changes of heat-cured mortars, Cement and Concrete Research, Vol. 31, pp.795-803, 2001
8) Divet, L. and Randriambololona, R.: Delayed ettringite formation: The effect of temperature and basicity on the interaction of sulfate and C-S-H phase, Cement and Concrete Research, Vol. 28, pp.357-363, 1998
9) Taylor, H.F.W., Famy, C., Scrivener, K.L.: Delayed ettringite formation -Review-, Cement and Concrete Research, Vol. 31, pp.683-693, 2001
10) Scherer, G. W.: Stress from crystallization of salt, Cement and Concrete Research, Vol. 34, No. 9,

pp.1613-1624, 2004

11) Flatt, R. and Scherer, G.W.: Thermodynamics of crystallization stresses in DEF, Cement and Concrete Research, Vol. 38, pp.325-336, 2008

12) Yuki Yamazaki, et al.: Effects of ASR on delayed ettringite formation (DEF), Japan Society of Civil Engineers 73rd Annual Meeting, pp.143-144, 2018

13) Zhang, Z., Olek, J. and Diamond, S., Studies on delayed ettringite formation in heat-cured mortars: II. Characteristics of cement that may be susceptible to DEF, Cement and Concrete Research, Vol. 32, No. 11, pp. 1737-1742, 2002

14) Kelham, S., The Effect of Cement Composition and Fineness on Expansion Associated With Delayed Ettringite Formation, Cement and Concrete Composites, Vol. 18, No. 3, pp.171-179, 1996

15) Barbarulo, R. et al.: Delayed ettringite formation symptoms on mortar induced by high temperature due to cement heat of hydration or late thermal cycle, Cement and Concrete Research, Vol. 35, pp.125-131, 2005

16) Ramlochan, T.: The effect of pozzolans and slag on the expansion of mortars and concrete cured at elevated temperature, Ph. D Thesis, Toronto University (2003)

17) Shoichi Ogawa, et al.: Study of controlling DEF using fly ash, Cement and Concrete, No. 864, 2019

18) Grattan-Bellew, P. E. et al..: Effect of Aggregate Particle Size and Composition on Expansion of Mortar Bars Due to Delayed Ettringite Formation, Cement and Concrete Research, Vol. 28, No. 8, pp.1147-1156, 1998

19) Bouzabata, H. et al.: Effects of restraint on expansion due to delayed ettringite formation, Cement and Concrete Research, Vol. 42, pp.1024-1031, 2012

20) Hime, W. G. et al.: Chemical and petrographic analyses and ASTM test procedures for the study of delayed ettringite formation, Cement, Concrete and Aggregates, Vol. 22, No. 2, pp.160-168, 2000

21) Johansen, V., Thaulow, N. and Skalny, J.: Simultaneous presence of alkali-silica gel and ettringite in concrete, Advances in Cement Research, Vol. 5, No. 17, pp.23-29, 1993

22) Thomas, M. et al.: Diagnosing delayed ettringite formation in concrete structures, Cement and Concrete Research, No. 38, pp.841-847, 2008

23) Odler, I. and Chen, Y.: Effect of cement composition on the expansion of heat-cured cement pastes, Cement and Concrete Research, Vol. 25, No. 4, pp.853-862, 1995

24) LCPC: LPC Test method No. 67; Internal sulfate reaction in concrete residual expansion test on concrete core extracted from the structure, 2009 (in French)

25) LCPC: LPC Test method No. 66; Reactivity of a concrete mix design with respect to delayed ettringite formation –Performance testing, 2007 (in French)

26) ACI: 201.2R-16 Guide to durable concrete, 2016.

27) Japan Society of Civil Engineers: 2016 Concrete Standard Specifications [construction edition], March 2017

28) Japan Society of Civil Engineers: Reinforced Concrete plant Product Design Construction Guidelines (draft), March 1969

29) Architectural Institute of Japan: The Japanese Architectural Standard Specifications JASS14 Curtain Wall Construction, March 2012

30) Godart, B. and Divet, L.: Lessons learned from structures damaged by delayed ettringite formation and the French prevention strategy, Proceedings of 5th International Conference on Forensic Engineering, 12p, 2013

31) Japan Cement Association: Common sense on cement, 2017