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The Effect of Secondary Ettringite Formation on the Durability of Concrete: A Literature Analysis

by Robert L. Day
KEYWORDS: accelerated testing, alkali-aggregate reaction, alkalis, calcium aluminates, calcium hydroxide, carboaluminates, carbonation, cement, cement chemistry, chlorides, chloroaluminates, cracking, delayed ettringite formation, Duggan Test, durability, ettringite, expansion, gypsum, heat treatment, hydration, ions in solution, microcracking, monosulphoaluminate, pH, pore solution, porosity, precast concrete, precuring period, preferred orientation, secondary ettringite formation, strength, sulfates, sulfate/aluminate ratio, swelling pressure, temperature, testing, thaumasite, railroad ties, transition zone.

ABSTRACT: The report comprises a review and analysis of the available literature pertaining to the causes, effects and prevention of secondary (delayed) ettringite in concrete. Over 300 publications have been examined. Case studies of damage in concrete possibly caused by secondary ettringite formation are examined first. Fundamental research on secondary ettringite formation, its chemistry, and deposition mechanisms is then reviewed. Key investigations on the topic are analyzed in detail. Next, the potential importance of (a) method of heat-curing and (b) the chemistry of cement is outlined. In the final chapter, a rapid test for evaluation of potential secondary ettringite susceptibility (the “Duggan” test) is evaluated. The analysis indicates that there appears to be a potential for a secondary ettringite formation problem in North America; it is highly probable that secondary ettringite formation can lead to significant deterioration of heat-treated concrete. However, it is unlikely that secondary ettringite formation is, or will be, the sole mechanism responsible for premature deterioration. The critical factors that determine extent of damage due to secondary ettringite formation are (a) duration of delay period before heating the concrete; (b) severity of the heating and/or cooling regime; and (c) the $SO_3/A_2O_3$ ratio of the cement. There is no evidence that non heat-treated concrete is susceptible to this phenomenon. Further research and improvements to the Duggan test may result in the development of a useful standard test method to assess the long-term dimensional stability and durability of concrete.


MOTS CLÉS: alcali, aluminate de calcium, béton préfabriqué, carboaluminate, carbonatation, ciment, chimie du ciment, chlorures, chloroaluminates, dormant de chemin de fer, durabilité, essai, essai accéléré, essai Duggan, ettringite, expansion, fissuration, formation retardée d'ettringite, formation secondaire d'ettringite, gypse, hydratation, hydroxyde de calcium, ions en solution, microfissuration, monosulfoaluminate, orientation préférentielle, PH, période avant cuit, porosité, pression de gonflement, rapport sulfate/aluminate, réaction alcali-granulat, résistance, solution de pore, sulfate, température, thaumasite, traitement à la chaleur, zone de transition.

RÉSUMÉ: Le rapport consiste en une revue et une analyse de la littérature disponible en ce qui a trait aux causes, aux effets et à la prévention de la formation secondaire (retardée) d'ettringite dans le béton. Plus de 300 publications ont été examinées. Des études de cas sur des bétons endommagés, possiblement à cause de la formation secondaire d'ettringite, ont été examinées en premier. La recherche fondamentale sur la formation retardée d'ettringite, sa chimie et ses mécanismes de dépôt est ensuite passée en revue. Les investigations d'importance sur le sujet sont analysées en détail. Puis, l'importance potentielle de (a) la méthode de cure à la chaleur et (b) la chimie du ciment est décrite. Dans le dernier chapitre, un essai accéléré pour évaluer le potentiel de formation retardée d'ettringite (l'essai "Duggan") est évalué. L'analyse indique qu'il est possible qu'il y ait des problèmes de formation secondaire d'ettringite en Amérique du Nord. Il est très probable que la formation secondaire d'ettringite produise une détérioration importante du béton traité à la chaleur. Cependant, il est très peu probable que la formation secondaire d'ettringite, soit ou devienne, le seul mécanisme responsable de détérioration prématurée. Les facteurs critiques qui déterminent l'ampleur des dommages dus à la formation secondaire d'ettringite sont (a) le délai avant chauffage du béton, (b) la sévérité du régime de chauffage ou de refroidissement et (c) le rapport $SO_3/A_2O_3$ du ciment. Il n'y a aucun indice à l'effet que le béton non chauffé soit susceptible à ce phénomène. D'autres recherches et des améliorations à l'essai Duggan pourraient mener à l'élaboration d'un essai normalisé utile pour déterminer la stabilité dimensionnelle à long terme et la durabilité du béton.


Cover Illustrations: Ettringite (white needle-like crystals) in concrete exposed to phenolphthalien stain; atmospheric steam-curing cycle; and precast structure under construction.
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Summary of Major Conclusions

A review and analysis was performed of available literature pertaining to the causes, effects and prevention of secondary, or delayed\(^1\), ettringite in concrete. Over 300 publications were examined. The principal findings from this project are:

- Given current cement-production and concrete-construction practices there appears to be a potential for a secondary ettringite formation problem in North America. It is highly probable that secondary ettringite formation can lead to significant deterioration of heat-treated concrete. The extent of the potential problem cannot be predicted with accuracy, but it is likely to involve a small fraction of the pre-cast concrete cast in North America.

- There is no evidence that secondary ettringite formation has been a principal cause of deterioration in non-heat-treated concrete. There is some suggestion that formation of ettringite after initial deterioration by other means can accelerate the deterioration process. Massive formations of ettringite observed in large cracks and pores appear, for the most part, to be innocuous.

- The critical factors that determine extent of damage due to secondary ettringite formation (all other factors being equal) are (a) duration of delay period prior to heating; (b) severity of the heating & cooling regime; (c) the $\frac{SO_3}{Al_2O_3}$ ratio of the cement.

- Use of cements with an $\frac{S}{A}$ ratio greater than about 0.7 or an $\frac{S^2}{A}$ ratio greater than about 2.0 may result in concrete which, under particular curing and exposure conditions, is susceptible to secondary ettringite formation and subsequent deterioration.

- Good quality laboratory research confirms that secondary ettringite formation can produce expansion and cracking of concrete made with certain North American commercial cements. In North America it is not unusual to find Type 30 cements with SO\(_3\) contents in the range 3.5 to 4.0\% — which could be as high as 4.5\%. It is not unusual to find alumina contents of 5\% or more and C\(_3A\) contents of 9\% or more. Calculation of the $\frac{S}{A}$ or $\frac{S^2}{A}$ ratios for such cements places them in the maximum expansion ranges determined by Heinz and Ludwig and by Gillott.

- Rapid heating and/or cooling and/or an inadequate delay period can result in microcracks — predominantly at the aggregate-paste or steel-paste interface. These cracks can act as nucleation sites for the later formation of ettringite.

- The aggregate-paste and steel-paste interface is a weak zone in the concrete that is high in both calcium hydroxide and ettringite contents. The ready availability of sulphates near the cracked interface provides pessimum conditions for secondary ettringite formation.

- The transition zone appears to be of higher quality when the interface involves limestone aggregate. This suggests that, all other factors being equal, concrete made with limestone aggregate may be less susceptible to secondary ettringite damage.

- Saturated, or almost saturated, concrete or concrete subjected to frequent wetting/drying cycles is essential to the formation of secondary ettringite and concrete damage.

- Early excessive heat treatments at temperatures above approximately 70\°C results in substantial amounts of sulphates being bound in an unusual form. These sulphates can be

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1 see Section 1.3 for an explanation of the terminology "secondary ettringite"
slowly released back into solution at later ages. This slow release process provides a supply of sulphate ions for secondary ettringite formation.

- The effect of secondary ettringite formation is substantially reduced by inclusion of an adequate air-entainment void system in the concrete.

- Where potential expansion due to secondary ettringite formation can occur, time to start of expansion increases and rate of expansion decreases as the size of the member or specimen increases.

- The 14 day sulphate expansion test does not provide an adequate prediction of cement stability at later ages.

- Specifications for Heat-Treated Concrete by the German Committee for Reinforced Concrete (Table 6.2) should be seriously considered for adoption in North America.

- A new test method to determine optimum gypsum content of cement should be developed which considers long-term stability of the cement as well as optimum strength and setting time.

- Further research and improvements to the Duggan test may result in the development of a useful standard test method to assess the long-term dimensional stability and durability of concrete.
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Notation

Where appropriate, cement chemists' notation has been used. This notation as it applies to the present report is:

\[ C = \text{CaO} \]
\[ S = \text{SiO}_2 \]
\[ \bar{S} = \text{SO}_3 \]
\[ A = \text{Al}_2\text{O}_3 \]
\[ H = \text{H}_2\text{O} \]
Chapter 1
Introduction

1.1 Objectives

At the March 15, 1991 meeting of a “Task Group on Secondary Ettringite Formation” — a group struck by the Canadian Standards Association Committee A5 (Hydraulic Cement) Executive — the following recommendation was made:

“Whereas the subcommittee is not aware of any documented cases of secondary ettringite failures in Canada, it is recommended that a detailed review and analysis of the literature (and especially the literature from Europe) should be undertaken to:

- attempt to identify significant factors which have caused documented cases of secondary ettringite failures in Europe
- attempt to determine which of the factors may be relevant to North America — i.e. is there, or is there likely to be, a potential secondary ettringite formation problem in North America?”

At the May 3, 1991 meeting of the CSA A5 Committee, the Committee passed the following motion in support of the Task Group’s recommendation:

“The A5 Hydraulic Cements Committee supports, in principle, the need for a detailed review and analysis of the literature relevant to secondary ettringite formation”. The Portland Cement Association agreed to provide the funding for such a study; this report is the result.

As well as the above objectives, the report centres upon an attempt to provide an adequate answer to a number of important questions concerning secondary ettringite formation:

- Is the occurrence of secondary ettringite and its effect adequately documented?
- What are the key properties of the constituents of concrete, the key properties of the concrete itself, and the key environmental parameters that determine whether secondary ettringite formation is likely to occur?
- What can be done in the cement and concrete industries in Canada to minimize the possibility that future construction will be prone to damage by secondary ettringite formation?
- Is a test available that can predict whether secondary ettringite formation for a given cement or concrete is likely to lead to durability problems?

The net result is a fairly comprehensive report. A database search indicated there were 440 references that may contain information relevant to the topic. Many of these references had obscure origins; although the interlibrary loans office of the University tried their hardest, only 327 references were reviewed. These 327 publications are listed at the end of this document. The 113 documents that could not be obtained are also listed. After review of these references not all were deemed to be directly relevant; in the report proper, approximately 160 of the 327 references are cited.

1.2 Outline of Report

The report starts with an examination of various case studies relevant to the formation of secondary ettringite in concrete. Many of the problems that have occurred centre upon the precast con-
crete industry; therefore, in Chapter 2 a summary of precast practices and relevant issues are given.

Chapter 3 looks at the fundamental processes associated with secondary ettringite formation. The chemistry and stability of sulphoaluminates are reviewed. The morphology and mechanisms of formation and expansion are studied in detail. Finally, chemical issues related to the formation of secondary ettringite are noted.

Chapter 4 is an examination of the physical processes associated with the deposition of ettringite which includes a review of the importance of the aggregate/cement-paste and steel/cement-paste interfaces.

Chapter 5 is an in-depth examination of the handful of key publications that directly relate to secondary ettringite formation and its consequences.

In Chapter 6 practical issues are discussed concerning the importance of gypsum and the chemistry of cement to the type and quantity of ettringite that is deposited. Also in Chapter 6 the types of heat-treatment are discussed; emphasis is placed upon specifications and guidelines that are intended to prevent "extreme" thermal treatments.

One of the principal conclusions of this report is that secondary ettringite formation could have a major effect in determining the long-term durability of some types of concrete. Accordingly, Chapter 7 concentrates upon an analysis of the Duggan test as a potential method to indicate the vulnerability of cements, aggregates and concretes to long-term deterioration mechanisms.

In Chapter 8 the major findings of the report are summarized and discussion centres upon the steps that might be taken by the construction industry to reduce the potential problem of secondary ettringite formation.

1.3 Terminology — "Secondary Ettringite"

One of the first questions that arose during the initial stages of writing this report was: what to call the phenomenon by which concrete, normally at ages of a few years or more, is damaged by the gradual formation of "ettringite" within the microstructure of the material. Lacking the imagination to invent a new term, the choice for the "appropriate" terminology was made among (1) delayed ettringite, (2) late ettringite and (3) secondary ettringite formation.

Study of the literature concerning fundamental mechanisms that cause the phenomenon leads to the conclusion that the term "delayed ettringite formation" is not accurate. This term implies that conditions within the microstructure might be suitable for the formation of ettringite but that ettringite does not form; this is not true. It also implies that the delayed ettringite that forms is the same ettringite that did not form during the early hydration of the cement; this is also not the case. "Late ettringite formation" is certainly more accurate in the practical sense, since the "problem" normally surfaces several years after the concrete is cast, but it is not precise. Late can have many meanings and, as study of this report will show, the process by which ettringite formation causes the problem occurs over a long time span. It is only the effect of the ettringite formation that comes to light "late".

The winner, then, is "secondary ettringite formation". It is accurate because materials engineers and chemists normally think of primary ettringite formation as the sulphoaluminate that forms shortly after gauging and that tends to disappear when sulphate ions in the pore solution become depleted. There can be a period for many concretes, and especially after heat treatment, where no
ettringite can be detected by X-ray analysis. Thus, the gradual growth of ettringite peaks on X-ray traces at later ages can naturally be thought of as the formation of secondary ettringite. The term also agrees with the first two definitions of “secondary” found in the Random House Dictionary: (1) next after the first in order, rank, or time; (2) not primary or original, but not with the third: (3) of minor or lesser importance.

Unfortunately, the decision on terminology will offend some. In geology, a “secondary mineral” is usually formed after the primary mineral has formed and then dissolved. In concrete this process may, in fact occur — in which case the terminology that has been chosen is accurate. Others would argue, however, that “the secondary formation of ettringite never did any concrete any harm”. As review of this report will show, the precise mechanism involved in the late expansion and cracking of concrete due to ettringite formation is far from being clearly defined.

The choice of the terminology “secondary ettringite” should not be taken as an implication that the author, at the outset, has taken sides concerning the fundamental mechanisms involved.

1 see, for example, a letter from B. Mather to C.R. Duggan of Feb 27, 1990 (also copied to ASTM committee C09.0202)
Chapter 2
Damage due to Secondary Ettringite Formation in Ordinary and Precast Concrete

2.1 Combinations of Attack Mechanisms

In 1965 Kennerley [161] was one of the first to report possible problems with delayed ettringite formation. He examined exudations at a cold-joint in the Roxburgh Dam, Otago, New Zealand. Analysis indicated that the white deposit was ettringite. Normally, when ettringite forms there is expansion, but he postulated that this expansion was avoided when constituents passed into solution, reacted and precipitated in the voids in the mass. If the solution was low in lime the solubility of both ettringite and calcium aluminates rose. Ettringite and calcium aluminates may therefore dissolve and be transported through permeable channels to areas high in lime; these compounds will then precipitate as ettringite in the lime-rich regions.

Pettifer and Nixon in 1980 [252] described several case studies where secondary ettringite may have played a part in the deterioration process.

- Concrete bases of some substations in the English midlands showed deterioration. Although there was alkali aggregate reaction, the researchers also observed pores and voids filled with ettringite and ettringite coating aggregate particles. This was surprising since there were only trace amounts of sulphates in the soil.

- Similar attack was noted in other substations in Western England and South Wales. The chert-containing limestone reacted, but cores also showed much ettringite co-existing with the gel reactant from the alkali aggregate reaction.

- Forty year old concrete blocks were examined which exhibited severe alkali-aggregate reaction and much leaching. These blocks were manufactured with unwashed beach gravel and were gauged with sea water. Upon petrographic examination, large amounts of calcite, gel, ettringite and “secondary portlandite” were observed. (Presumably by “secondary portlandite” the researchers mean CH deposited in the pores of the microstructure).

- The Pirow Street Bridge in Cape town, South Africa showed cracking only 4 years after completion, and remedial repairs were necessary after 9 years. Potentially reactive aggregates were used, but a low alkali cement was also used. A significant feature of the petrographic examination was a yellowish gel accompanied by moderate amounts of ettringite.

Around the same time, Volkwein [314] examined 12 to 80 year old concrete bridges for carbonation, chloride penetration, deterioration and corrosion. As Figure 2.1 shows, the depth of carbonation was highly variable (the low carbonation in the 80 year old concrete was because it was made with Roman cement). The carbonation depth depended greatly on the moisture condition of the structure during its life. Carbonation assisted the penetration of ions into the concrete since it was found that carbonated concrete conducted vapour “about twice as well” as non-carbonated concrete. On bridges, penetration of chloride into the top of decks was negligible; most Cl penetrated via seeping, splashing and wind-borne Cl carried to the concrete understructure. Such processes can result in the chloride ion penetrating up to 50mm in sound concrete and up to 90mm in frost damaged concrete. Figure 2.2 shows examples of the penetration depth and Cl ion concentrations for various ages and qualities of concrete.

Volkwein found that in these deteriorated concretes, highly contaminated by Cl, “remarkable” accumulations of needle-shaped crystals were found, “particularly in cracks, pores and around ag-
CARBONATION DEPTHS OF DRY CONCRETE FROM BRIDGE STRUCTURES

Figure 2.1
Carbonation of Bridge Structures [data from ref. 314]

Chloride Penetration into Concrete Close to Road -- Due to Splashing

Figure 2.2
Chloride Penetration into Concrete due to Splashing Action [data from ref. 314]
gregates". These crystals were analyzed and were found to be ettringite, with some thaumasite.

Volkwein postulated that since the sulphate content had not changed, then the "chlorides did cause the formation of ettringite" from the sulphate in the cement. Additional reactions occur other than the formation of Friedel's (monochloroaluminate) salt due to the penetration of chlorides. Wetting and drying also helps to transport soluble cement compounds to preferred locations. Volkwein noted that "it cannot be said whether these ettringite crystals had caused the deterioration of concrete or had grown up in already open cracks".

Volkwein's results are most interesting because ettringite appears to have formed in a chloride rich environment. Contrast this with the laboratory results of Attiogbe et al [12] who found that during an accelerated exposure test, secondary ettringite would not form while concrete prisms were soaked in a sodium-chloride saturated solution. Other research confirms that ettringite decomposes in sodium chloride solution [243-245].

Jones & Poole in 1987 [154] looked at the effects of alkali-silica reaction on 3 structures in the United Kingdom. They examined 20mm thick disks from concrete cores taken from the structures. The disks were stored in sealed containers at constant temperatures of 1, 15, 20, 25 and 38°C and relative humidities of 65, 75, 85 and 100%. Expansions were measured; since the concretes were taken from structures, all expansions noted were relative to the unknown deformation of the structures.

These researchers found that initial expansion proceeded faster at elevated temperature but the rate declined more rapidly. The final expansions were roughly inversely proportional to storage temperature. Petrographic examination did not reveal the classic alkali-silica (asr) reaction rims that are commonly observed. Cracks were often observed around "aggregate margins" which radiate into the paste matrix. Asr product was rarely seen infilling the cracks, but was most often seen at the centre of reactive particles. In one structure, large quantities of ettringite were observed. This material was coarsely crystalline and was seen infilling the microcracks and "lining voids". Ettringite often appeared to have replaced previously deposited silica gel.

Jones & Poole noted the research of Greening [120] who showed that monosulphate becomes metastable in the presence of CaCO$_3$ and reverts to ettringite$^2$. The researchers proposed that the presence of limestone aggregate provided the calcite which rendered ettringite the stable sulphate phase. Ettringite, initially dispersed throughout the microstructure recrystallizes into a coarsely crystalline form. The process is helped by increased permeability caused by other accompanying processes such as asr cracking. The formation of ettringite in the voids is thus due to a through solution process through the pore fluid. The "preferential recrystallization" of ettringite in "gel-filled" microcracks may contribute to the overall deterioration process.

El-Sayed [96] did a post-mortem on 7 deteriorated reinforced concrete structures in a marine environment in Egypt. Ettringite was observed in 3 of the 7 concretes. He concluded that a combination of factors ultimately contribute to premature deterioration.

Most experimental research necessarily attempts to isolate one or two variables and examines the effects of controlled variations on behaviour. As El-Sayed notes, the real situation is far different. It is hard to imagine a practical situation where, over the course of several years, only one mechanism is responsible for concrete deterioration.

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1 See Section 3.8 for more information on the role of chloroaluminates

2 The role of carbonates in the formation and effect of secondary ettringite is given in Section 3.7.2
2.2 Petrographic Observations

One of the common observations of damaged structures is the occurrence of localized formations of ettringite. For example, Chandra and Berntsson [48] examined damage in the back-lining of swimming pools in the south of Sweden. The concrete lining was 15 years old. They observed both translucent and opaque fibres and “white particles” on surfaces; in spots there was a white precipitate. Analysis confirmed asr, but ettringite was also present, along with calcium hydroxide, calcite and gypsum which had been leached to the surface. The diagnosis was that deterioration was “caused by a combination of interacting factors” including alkali silica reaction, aggressive reaction of sulphates, and alteration of the feldspar aggregate [55].

Macleod et al [245] examined damage of a concrete bridge in Strathclyde, Scotland. They observed the presence of “white spheres” in the microstructure, ranging in diameter of 1 to 4mm, which had grown preferentially within the spherical voids of the concrete (air-entrained voids). X-ray analysis identified this material as ettringite, with a small amount of gypsum and “an unidentified chlorine-rich phase”. This material was clearly a secondary alteration product.

Ozol [249] performed petrographic examinations of concrete attacked by alkali-silica reaction which revealed “desiccated gel balls” up to 7mm in diameter adjacent to aggregate particles. Fine crystals of ettringite were incorporated into these balls. Ettringite was also found to be present in cracks and in coarse-aggregate sockets; sometimes it was found by itself and other times it was found “in association with” dried asr gel-reaction product.

Neck [237] noted a common feature of damaged concrete that has been extensively heat treated and exposed to weathering is the “secondary phases” that seem to form at the contact zone between the matrix and the aggregate. These phases appear to be ettringite or thaumasite or mixed crystals.

Sylla [297] performed microscopic examinations of samples of cracked concrete. He found the cracks to be almost completely filled with needle-shaped reaction products. The needles were all orientated vertically to either the aggregate or crack surface. It appeared from the observations that the crystals grew in a uniform front into the crack (suggesting a topochemical reaction mechanism). Once the crack is full then further transport of ions and growth may result in an increase in crystallization pressure and further damage. Sylla postulates that the initial cracks are “pre-existing” as a result of cracking during thermal treatment.

2.3 Problems with Precast Concrete and Ties

In a Research Institute document [268], problems prior to 1984 are reported to have occurred in Germany with heat-treated prefabricated concrete elements, and especially railway ties and cladding panels. The problem initiates as crack formation at corners and edges which then tend to extend into the interior. More severe separation of aggregate from the paste matrix then follows. Petrographic examination of the cracks almost always shows infilling with thaumasite or thaumasite/ettringite mixed crystals. It appears that the thaumasite/ettringite mixture forms in already existing cracks. The report notes that heat-treatment has two important effects to initiate these problems:

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1 See Section 3.10 for a description of reaction and expansion mechanisms of ettringite
an inadequate pre-treatment allows internal damage through debonding between aggregate particles and the paste matrix, and through cracking.

heat treatment interrupts the normal formation of ettringite; this formation continues later in the hardened concrete, with undesirable results.

It was noted that the solution to the problem is to provide an adequate period for precuring. Tepponen [303] reported the Scandinavian experience with problems of production of railway sleepers (ties) that have occurred since the 1960s. Ties were manufactured in the 60s and 70s with high early strength cement (approximately 4% SO₃ and 8% C₃A). The fineness of cements was in the range 460-480 m²/kg. The cement content of the concrete mix was approximately 400 kg/m³ and the water cement ratio varied from 0.36 to 0.39. Ties were manufactured with either a 1 or 2 hour delay period¹ and a maximum temperature in the range 75-80°C. The soaking period was 2.5 or 4 hours. One-day strength of the 1965 ties was 56 MPa, and was 43 MPa in the 1971 ties.

Tepponen noted that the ties showed visible damage after 15 years. Thin-section analysis showed partial filling of the microcracks in the ties that showed cracks. The more deteriorated ties had all the pores and some of the larger cracks filled with microcrystalline ettringite which had accumulated in the free space. In the more severely damaged concrete the bond between paste and aggregate was poor. Further studies in 1970 confirmed that the main reason for deterioration was, however, the poor frost resistance of the concrete. To solve this problem air content was increased and the maximum heat-treatment temperature was reduced to 60°C.

New studies performed in 1980 revealed that “microcracks...are the primary cause of deterioration” [303]. These cracks occur due to frost, load, premature heating, improper heat treatment, too severe or rapid heat treatment, etc. If temperature is also greater than 70°C during curing, then “metastable monosulphate” is produced which forms ettringite when (a) the temperature drops back to normal and (b) sufficient water is supplied.

New production methods were adopted in the 1980s which employed new German guidelines² for heat treatment. These consist of a prestorage period of 3 hours, a rate of temperature rise between 10-15°C/hr and a maximum temperature between 65-70°C. Little changes in the cement composition were made and, in fact, the new cement that was used had a higher aluminate and thus C₃A content (12% in 1980 vs. 8% in 1965). One possibly significant change was the reduction in the maximum size aggregate from 32 to 16mm. The new concrete strength at 1 day was 68 MPa. Tepponen reports that the ties have been in service for 5 years and no expansion has been observed even though microcracks due to stress are present [303].

Heinz and Ludwigs’s experiments [132], discussed in detail in Sections 5.3 and 5.5, were prompted by practical problems that surfaced with precast units — specifically cladding panels and precast units. These high-strength structural elements were heat-treated during production. Damage surfaced after several years’ exposure to “open-air weathering” where there was frequent saturation. Cracks were first observed around edges, followed by further cracking and loss of bond between the paste matrix and coarse aggregate particles.

In another publication, Heinz and Ludwig [133] noted occurrences of damage in Europe of high-strength precast units which used Type 55 high-early-strength Portland cement. These members were heat-treated in production. Damage always occurred on units exposed to the weather and

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¹ also called “pre-storage” or “preset” — the time between casting and the start of thermal treatment
² See Section 6.3 for a discussion of precast specifications
subjected to frequent moisture saturation. The damage was attributed to the reformation of ettringite following heat-treatment.

Testing at the British Cement Association [177] to examine the importance of secondary ettringite formation was prompted by problems with site concretes in Germany and Finland, and particularly with deterioration of rail ties. In the U.K. there have been a few cases of damage of particular prestressed and reinforced concrete bridge beams that have cracked at a late age due to "ettringite crystallization".

In particular, 15 prestressed and reinforced concrete beams were examined that were cast between 1963 and 1969 [177]. These beams cracked due to "unexplained causes". All were cast using high early strength cement, and all were probably steam-cured. The cement content was greater than 450 kg/m³ in all concretes. The cracks took as long as 15 years to appear. The problem was initially thought to be due to alkali-silica reaction, but examination of thin sections showed dense bands of ettringite, 25 μm thick, around coarse aggregate grains. In uncracked sections there were thinner layers of ettringite around aggregate particles.

Ettringite has been observed in normally-cast structures which, in most cases, have been damaged by a combination of factors. In such structures ettringite appears capable of being a contributory cause of destruction, but unless an ample source of external sulphates is provided does not appear to be able to instigate substantial destruction. On the other hand, case studies which have examined deterioration of precast concrete, and many examinations to be described in following sections, strongly indicate that secondary ettringite formation can be the main cause of destruction once the heat-treatment process has established the nucleation sites for ettringite to form. Accordingly, it is appropriate at this point to examine the precast concrete process.

## 2.4 Precast Concrete

### 2.4.1 Effect of Heat Treatment on Properties

It is clear from the literature that the main reason accelerated-curing régimes were devised for precast concrete was to accelerate the strength sufficiently that production of structural elements could be performed on a one day cycle. Economic pressures provided encouragement to obtain a strength sufficient to allow release of prestress; this value varied for different applications, but in general the 18 hour to 1 day target strengths were in the range 27-31 MPa [129, 184, 218]. Until the 1980's, strength development and the result of accelerated curing on both early and later-age strengths were the prime objectives of the research.

In 1951, Saul [278] noted that from 1921 to the time of his writing considerable controversy and conflicting research had occurred concerning steam-curing. He noted that there had been little agreement on optimum curing temperature, duration of treatment, delay period, etc.

Saul found with his own research that the most important factor influencing the ultimate strength of the concrete was the rate of temperature rise. He reported that good results could be achieved if the concrete temperature did not reach 50°C until 2 hours after casting, and 100°C until 6 hours after casting. Saul criticized some commercial operations because they used too rapid temperature rises, but noted that this is satisfactory if a suitable delay (preset) is employed prior to the start of heating. Saul noted that very rapid temperature rise can be used if very high early strengths are needed, but 7 and 28 day strengths may suffer by as much as 1/3 (when compared to a normally cured control); later, others came to similar conclusions [e.g. 321]. The effect of heat-treatment, and especially 100°C treatment, on durability of concrete is not a theme that is considered by Saul — or by any of the early research on precast concrete. There is no indication
that concretes manufactured with the aggregates and cements available at the time showed any long-term distress.

Chamberlin [47] was another early researcher of precast concrete. He observed that steam-curing between temperatures of 85 and 93°C caused severe damage to the concrete when delay periods were too short. Furthermore, subsequent strength gain was small. On the other hand, concretes treated at 74°C were as strong as the control concretes at 28 days. Based on these results, it was concluded that a delay period of "several hours" is required after casting, and a maximum temperature rise of less than 22°C/hr is necessary if it is desired to prevent damage to concretes steam-cured at temperatures greater than 74°C.

Plowman [256] confirmed that the low strengths of heat-cured concrete at later age was a well-established phenomenon; ultimate strength is influenced by the rate of early hydration. It only takes a high temperature for the first few hours of hydration to reduce ultimate strengths significantly.

The work of Klieger in the late 50's and early 60's [164-166] firmly established the pros and cons of the heat-treatment procedure. Fairly moderate curing temperatures from 4.4 to 49°C were used by Klieger in his research. The strength at 1 day of the 49°C cured concrete was 178% that of the control concrete cured at 23°C. Later-age strengths were somewhat reduced but "no retrogression in strength occurs with age". Klieger suggested that an acceptable heat-curing cycle consisted of 3-6 hours delay period, a 16 hour heating period and then gradual cooling over 3 hours to avoid excessive drying.

Klieger also found that elevated curing temperatures affected flexural strength in a similar manner to compressive strength; although initial strengths were higher the concretes that were tested exhibited considerably lower strengths at 3 months and 1 year [165].

In one of the few examinations of durability, Klieger observed that curing at elevated temperature of concrete made with high-early-strength cement does not hinder freeze-thaw durability if the concrete is dried prior to exposure. Klieger suggested that a few days of drying in the yard is enough to accomplish sufficient drying. He also found that concretes cured at elevated temperature in a 24 hour cycle show less drying creep and shrinkage under sustained stress than those cured at normal temperatures [166].

Hanson [128] also noted that accelerated curing causes significant reductions in creep and shrinkage. This has important influences on the magnitude of prestress loss which can be reduced by as much as 40% if heat-treatment is used. The author suggested that a heat-treatment régime consisting of 4-6 hours delay period followed by a 17°C/hour temperature rise to 66°C and a soaking period of 13 hours is about optimum with respect to strength development.

In a subsequent paper, Hanson examined the properties of lightweight concrete [127]. The optimum conditions for steam-curing lightweight concrete were not substantially different than those for normal-weight concrete, this was confirmed by other research [185]. It was also found that lightweight concrete is less susceptible to damage if severe heat-treatments are used (too high temperature, too rapid temperature increase, insufficient delay period). This is probably due to the high elasticity of lightweight concrete enabling it to absorb better the internal strain that occurs upon heating.

Merritt and Johnson [218] determined the strength of various heat-treated concretes. Soaking time and soaking temperature were the main variables. A summary of the results is given in Figure 2.3. For all conditions heat-treatment resulted in a strength immediately after treatment that was greater than the fog-cured concrete. The 7 and 28-day strengths were always less than control. Note, however, that the delay period for all casts was very short (0-0.5 hours). At this short preset the optimum curing régime, both mechanically and financially, appears to be a soaking time of 18 hours within a temperature range of 52-66°C.
Australian experience indicated that a premature application of steam can reduce the compressive strength at later ages by up to 20%. An optimum delay period between 3-5 hours is appropriate for temperature gradients from 10-40°C/hour. If an adequate delay period is used, then subsequent strength development is directly related to the maturity. However, with a proper delay and moderate temperature rise the 28 day strengths of heat-cured concretes can exceed those of standard-cured concretes [184].

Farsky noted that after a plastic strength of 1 to 1.5 MPa is achieved in the concrete the speed of heating does not influence strength. The period of delay prior to heating is, however, a decisive influence on later strength development. He proposed that a reasonable period of delay would be the time to initial set of the cement [100].

Some researchers have suggested that tailoring the cement chemistry or the use of chemical admixtures can help to reduce the problem with low ultimate strengths. Saul [278] suggested that the adverse effect on strength due to a rapid temperature rise during pretreatment can be compensated for by additions of calcium sulphate or alkali to the mix.

It was also proposed that the use of a superplasticizer can permit as much as a 25% reduction in the water content of precast, heat-treated concrete. As a result, the normally observed reduction in long-term strengths can be avoided. Concrete cast with w/c=0.3 through the use of a superplasticizer resulted in a 43% greater strength at 28 days than a normally-cured, superplasticizer free, equivalent Type I concrete [254].
Pfeifer and Marusin [255] observed that the compressive strength of heat-cured concrete was greatly affected by the chemical composition of the cement. With respect to optimizing 1 day strength, they proposed that the best chemical composition is one with: (a) C₃S:C₂S = 3:1; (b) C₃A:C₄AF = 2:1; (c) C₃A = 10-15%; (d) SO₃ = 5-7%. This is similar to a standard Type 30 cement except for the higher SO₃ content. For optimum high early strength "the SO₃ content should be as high as allowed"; current ASTM specifications allow a maximum of 4.5% SO₃, but "early-age strengths can be dramatically increased during heat curing by using somewhat higher SO₃ contents than currently allowed by ASTM C150".¹

It is important to note that although strength has been the primary property investigated, long-term strength is not the only property that suffers by inadequate heat-curing. For example, a short steam-cure at 54°C followed by drying resulted in a 4000% increase in permeability when compared to a water-cured control specimen [135]. This is shown in Figure 2.4. All steam-cured concrete resulted in an increase in permeability. Fog-curing after heat-treatment is beneficial since it results in a decrease of permeability measured at 28 days.

![Figure 2.4](image)

**Figure 2.4**
Effect of Heat-Curing and Drying on Relative Permeability [data from ref. 135]

¹ Note that there is no mention of long-term properties in this document. The proposal by the researchers to use as much SO₃ as possible is, in this author's opinion, indicative of the acceptance of strength as the universal quality indicator that predominated in the industry until recently. Fortunately we are now learning very quickly that adherence to that philosophy often leads to inferior concrete in the long term—with resultant costly repairs.
2.4.2 The Cause of Insufficient Strength Gain after Heat Treatment

Hansom, in 1963, noted that microstructural damage is caused during a short pre-steaming period, especially when the heating rate is high. Cracks that occur are due to the action of tensile stresses caused by a rapid heating rate and resultant stress distributions that occur across the specimen or structural member. The greatest cause of these stresses is probably the much larger expansion coefficient of free water when compared to the solid ingredients of the concrete. To avoid this damage, Hanson suggests an optimum curing period consists of 5 hours delay, a temperature rise at 22°C/hr, and a maximum constant temperature of 66°C held until steam shutoff at 18 hours; this allows 6 hours for form stripping and readying for the next run [129].

Alexanderson [7] proposed other techniques that could be used to minimize the effects of damage associated with expansions and cracking:

- resisting pore pressures—through the use of closed forms, or by letting the concrete attain a minimum strength before the start of heating;
- eliminating pore pressure—by heating the concrete ingredients before casting or by eliminating air voids;
- letting the concrete crack—and repairing it, perhaps by vibrations after heating.

Others have also attributed damage to the principal mechanism of differential thermal expansions. Sylla [297] stated that differential thermal expansion appears to be the primary cause of cracking during thermal treatment. Water is a key component in this regard because it has an expansion coefficient about 10 times greater than any of the solids. Sylla hypothesized that premature heating causes large expansions in the thin layer of water that coats the aggregate particles at casting. If heating is delayed somewhat then some of the water in this layer is removed due to hydration; also the concrete has some stability so that the overall damage is less.

Soroka et al [292] listed three reasons to explain why heat-curing causes a reduction in later-age strengths when compared to a normally-cured control.

- The first hypothesis was proposed by Verbeck and Helmuth [312]. Due to heat-treatment, the paste microstructure is more heterogeneous because of the very rapid rate of initial hydration. Ample time is not allowed for hydration products to diffuse away and precipitate in the space between cement grains. A dense hydrate forms near the cement grains and a weaker gel and more interstitial space occur away from the grains. Cement hydration at later ages is also retarded because of the denser layer of hydrate surrounding the unhydrated grains

- Temperature appears to change the morphology of C-S-H gel particles. Heat treatment reduces the relative amount of long C-S-H particles to short particles. It is not entirely clear why this should have a profound effect on strength development.

- Rapid heating results in differential thermal expansions and cracking—thus, damage is produced.

To examine this reduction in strength, concrete was steam cured after a 30 minute delay period. The treatment temperatures were either 60 or 80°C and were held for periods ranging from 2 hours to 4 hours:40 minutes (Figure 2.5). For some specimens (Cure 3) no further moisture was provided (65% r.h.) after heat-treatment until specimens were tested at 28 days. In Cure 2, specimens were water cured after heat-treatment until 7 days and then placed at 65% r.h. until 28 days. Control specimens (Cure 1) were treated like Cure 2 specimens except there was no heat-treatment. The results given in Figure 2.5 indicate that lower strengths may not be due to damage during heat treatment, but may be due to inadequate curing after the heat treatment.
Cure 1 = Water cure at 20 °C for 7 days, then at 65% rh until test at 28 days
Cure 2 = Heat cure at given T after 30 minutes delay, followed by water cure at
20°C until 7 days, 65% rh to 28 days
Cure 3 = Heat Cure of Cure 2, no water cure,

\[\text{Strength as } \% \text{ of Standard Cure}\]

\[\text{CURE 2} \quad \text{CURE 3}\]

\[\% \text{ OF CURE 1} \quad \% \text{ OF CURE 1}\]

**Figure 2.5**
Effect of Post-Treatment Water-Curing on Strength Gain [data from ref. 292]

Most researchers blame the presence of water and its large thermal expansion coefficient as the reason why damage occurs. However, Pfeifer & Marusin [255] propose that one must be especially careful when air-entrainment is present. Moist air expands in the pores during heating, so even if the air content is as low as 1%, cracking can develop under certain conditions. Above 43°C a delay period is not necessary as long as temperature rise is gradual. At 60°C, the delay period should be 4.5 hours, and at a 90°C heat-treatment temperature, the delay period should be approximately 6 hours. The delay period can be reduced if the initial temperature of the raw materials is increased, thus increasing early tensile strength gain and reducing the volume expansion of the various components.

### 2.5 Comment

The heat-treatment régimes for the precast industry appear to have evolved with one over-riding consideration — to obtain the highest strength possible in the shortest time. When engineers devised régimes to do this they quickly realized that later age strengths could be substantially less than that of a normal-cured concrete. If later age strength was not important, then a certain amount of cracking during the heat-treatment process was accepted. There appears to have been little concern or, perhaps, appreciation that long-term durability of the cracked material could be an issue. The chemistry and physical properties of cement in the 50's and 60's were significantly...
different than now; it may be that during this period strength was a much stronger indicator of overall quality than it is at present.

Most concrete manufacturers appear to have searched for a compromise: to develop a heat-treatment regime that would still produce high early strengths but which would not result in large comparative strength reductions at later ages. To do this it was realized that the rate of temperature rise had to be low and/or there had to be a significant delay period between the time of casting and the start of heating. As will be shown in the following chapters, there is a third important factor that must be considered if both acceptable early- and late-strengths and long-term durability are to be ensured — the maximum curing temperature.

The deterioration of concrete in the field will almost always be a combination of influences, including freeze/thaw, corrosion, alkali-aggregate reaction, stress cracking, sulphate attack, carbonation, secondary ettringite formation and a number of other possible processes. The mechanisms by which the overall deterioration process advances is extremely complex and probably beyond any model that could be tested in the laboratory or on a computer.

Nevertheless, particular processes can be recognized and we can ensure that the influence of those processes in the overall deterioration scheme are minimized. Corrosion and sulphate attack are two examples where simple steps have been taken to ensure, at least on paper, that their effects will be minimized.

Recently, several researchers in Europe (see Chapter 5 as well as this chapter) have provided strong evidence that under the right conditions secondary ettringite formation may be a significant factor in influencing the long-term durability of some types of concrete. Like corrosion and sulphate attack, steps can be taken to help ensure that secondary ettringite formation is either an insignificant or only a minor influence; some of these steps can be discerned from reading the material to follow.

At the moment, secondary ettringite formation is different in one key aspect when compared to corrosion and sulphate attack; it is by no means as widespread in occurrence. Nevertheless, it may become a very important consideration if its potential is ignored. It should, however, be kept in mind that at present the proportion of damaged concrete where damage has been directly attributed to secondary ettringite formation is a very small proportion of all precast concrete cast in Europe and North America.
Chapter 3
SECONDARY ETTRINGITE FORMATION:
FUNDAMENTAL RESEARCH

3.1 Overview of the Cement Hydration Process.

This report assumes that the reader has a working knowledge of the chemistry of cement and cement hydration; therefore, no attempt is made to perform a detailed review. The reader is referred to the excellent reference book by Taylor [302] for comprehensive information on all aspects of the properties of cement.

The formation and consequences of formation of ettringite are the principal topics of this report. In a normal modern cement, ettringite forms due to the reaction between gypsum and calcium aluminate. X-ray peaks that are associated with ettringite are detectable within a few hours and the quantity increases during the first day. After this time the ettringite peaks normally weaken, but, depending upon the chemistry of the cement and the environmental conditions, ettringite may persist indefinitely. It is a general belief that if all of the gypsum is consumed through the ettringite reaction, ettringite converts to monosulphoaluminate. In an average cement this conversion process starts at about 1 day and can be monitored as a reduction in the size of the ettringite X-ray peaks. Much of the monosulphoaluminate phase that forms instead is poorly crystalline [302].

3.2 Early Formation of Sulphoaluminates

The commonly held chemical formula for ettringite is:

\[ 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \] or in chemists' notation is: \( C_6\Sigma_3H_{32} \)

and for monosulphate is:

\[ 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O \] or: \( C_4A\Sigma_{12} \)

The reaction that occurs between C\(_3\)A and gypsum can be found in numerous texts:

\[ C_3A + 3C\Sigma H_2 + H_2O \rightarrow C_6\Sigma_3H_{32} \]

Except for the unusual combination of very low C\(_3\)A contents and high gypsum contents, the gypsum will be used up by this reaction before the C\(_3\)A. When this occurs, the remaining C\(_3\)A will take part in a reaction whereby ettringite decomposes to monosulphoaluminate:

\[ 2C_3A + C_6\Sigma_3H_{32} + H_4 \rightarrow 3C_4A\Sigma_{12} \]

Thus, in the net reaction, 3 moles of C\(_3\)A and 3 moles of gypsum will produce 3 moles of monosulphoaluminate. Use of the Bogue equation and performing stoichiometric calculations from the formulae above, one can calculate the SO\(_3\)/Al\(_2\)O\(_3\) mass or molar ratios (S/A ratios) required to consume all of the C\(_3\)A and convert it to monosulphoaluminate. Figure 3.1 shows the dependence of this ratio on the C\(_3\)A content of the cement (given an assumed Fe\(_2\)O\(_3\) content of 3%). If the S/A ratio is greater than the value shown, C\(_3\)A will still be available after all of the ettringite has been consumed; the remaining C\(_3\)A will react with calcium hydroxide and water to produce C\(_4\)AH\(_{13}\) [302]. The above analysis is highly idealized. It is important to recognize, however, that the conditions under which ettringite forms, and the structure of ettringite itself are highly complex.
3.3 Crystal Structure and Composition of Ettringite

The use of the term "ettringite" without qualification normally refers to "sulphate ettringite", which has the formula $C_6A_3S_3H_32$. However, it should be noted that "ettringite" is, in fact, a general term used to denote a number of minerals, all with very similar crystal structures. McConnell & Murdoch [202, 203], for example, noted in 1962 that ettringite should be represented by the general formula:

$$16[A_d(XO_4)_3(H_2O)_{12}]$$

where "A" represents six-fold coordinated atoms (Ca, Na, Al), and "X" are four-fold coordinated atoms (S, Si, H_4 and also some Al). The formula is written to make clear the interchangeability of the various ions.

Moore & Taylor [231] wrote the formula for ettringite in a different way, again in an attempt to clarify all of the various substitution of ions that can occur, but also to illustrate the crystal structure of this class of material:

$$Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O$$
The researchers noted that the crystal structure is based on columns with composition

$$[\text{Ca}_3[\text{Al(OH)}_6]\cdot12\text{H}_2\text{O}]^{3+}$$

which run parallel to the c, or needle, axis. The sulphate and remaining water molecules lie between the columns.

Taylor [300] provided a very clear picture of the ettringite-group crystal structure which is characterized by four positively charged columns in a trigonal structure, between which occur channels which contain anions and sometimes water molecules. Figure 3.2 shows the sulphate-ettringite structure. The a and b lattice dimensions are 11.23Å, while the repeat dimension in the c direction is 10.7Å.

Two other minerals which closely parallel the ettringite structure, and are of interest to concrete researchers are thaumasite and jouravskite. The parallel structures can be clearly seen in the chemical formulae:

- ettringite: $$[\text{Ca}_3[\text{Al(OH)}_6]\cdot24\text{H}_2\text{O}]\cdot(\text{SO}_4)_3\cdot2\text{H}_2\text{O}$$
- thaumasite: $$[\text{Ca}_3[\text{Si(OH)}_6]\cdot24\text{H}_2\text{O}]\cdot(\text{SO}_4)_3\cdot(\text{CO}_3)_2$$
- jouravskite: $$[\text{Ca}_3[\text{Mn(OH)}_6]\cdot24\text{H}_2\text{O}]\cdot(\text{SO}_4)_3\cdot(\text{CO}_3)_2$$

In thaumasite, silicon replaces aluminium in the columns (Figure 3.2), while in jouravskite manganese replaces aluminium. For both thaumasite and jouravskite water molecules contained between the columns of the ettringite structure are replaced by carbonate.

In fact, Taylor [300] notes that partial or complete replacement of sulphate ions can occur with CO$_3^{2-}$, CrO$_4^{2-}$, Cl$^-$, and IO$_3$-. The aluminium, on the other hand can be replaced by Ti, Cr, Mn, Fe, or Ga. The calcium can be replaced by strontium. Other researchers [196, 326] have confirmed the wide variety of ions that can replace aluminium and/or sulphate. More recent research [130, 171] has also shown that oxyanions such as arsenate, borate, chromate, molybdate, selenate and vanadate may substitute for sulphate in the ettringite structure.

Taylor [300], expanding on earlier work re-defined the composition of the column per half unit cell in sulphate-ettringite as $$[\text{Ca}_3[\text{Al(OH)}_6]\cdot24\text{H}_2\text{O}]^{6+}$$, while the material in the ettringite channels is $$[\text{SO}_4]^3\cdot2\text{H}_2\text{O}]^{6-}$$ to make the entire structure electrically neutral. He noted that each column is of nearly cylindrical shape and its surface is comprised entirely of water molecules, “or more accurately the H atoms that these contain”.

It has also been shown that various ions can replace sulphate in monosulphoaluminate. The wide variety of chemical compositions of both compound types has prompted the use of the terms (a) “AFt” for Aluminate-Ferrite-trisubstituted — the “needle-like hexagonal hydration products which crystallize with 3 molecules of a calcium salt per molecule of C$_3$A”; and (b) “AFm” notation to stand for Aluminate-Ferrite-monosubstituted compounds, which are hexagonal or pseudo-hexagonal plates which contain one molecule of a calcium salt per molecule of C$_3$A [163].

3.4 The Role of Ettringite in the Retardation of the Calcium Aluminates

Gypsum is added to Portland cement clinker to retard the rapid hydration of the calcium aluminates. Lerch [180] outlined the mechanism of retardation of aluminates by sulphates. When water first contacts cement there is an initial rapid dissolution of anhydrous aluminates and rapid crystallization of hydrated calcium aluminates. This occurs before the solution becomes saturated.
Figure 3.2
Sulphate-Ettringite Crystal Structure [extracted from Taylor [300] and annotated]

Structure of Columns in Ettringite Crystal
Part of Single Column Projection
Blank Circles are Water Molecules

Plan View, Showing Columns and Channels

Lattice a dimension = 11.23 Å

Lattice b dimension = 11.23 Å

SO₄²⁻ and Water Molecules Located in Channels Between Columns
with lime and gypsum and corresponds to the first peak in the heat of hydration curve. Since lime and gypsum in solution decrease aluminate solubility, the rate of formation of aluminate decreases as more of these materials are dissolved (lime alone is not sufficient to retard the hydration of aluminates). Once a saturated lime/sulphate solution is achieved, aluminates continue to hydrate more slowly. Calcium silicates dissolve and form C-S-H. Sulphoaluminates start to form. Because of the formation of sulphoaluminates, the gypsum eventually becomes depleted and the concentration of sulphates in solution starts to drop. The solubility of alumina again rises and a rapid aluminate reaction begins again.

Another theory attributes retardation to the direct formation of a coating of ettringite on the surface of calcium aluminate grains [69]. The retardation mechanism of gypsum is more effective in the presence of CH since ettringite crystals are more fine-grained and can therefore coat the surface better. Some later research, however, has questioned whether a sufficient amount of ettringite can deposit in a short time to have the pronounced retardation effect that is observed [206].

Although there has been no convincing explanation of the retardation mechanism, fairly convincing evidence does exist that ettringite forms by a through-solution mechanism. There has been much controversy about this over the years, and various schools of thought have formed about whether formation is through solution [e.g. 134] or topo-chemical. There is also some suggestion that formation may be due to a combination of mechanisms: the first is a through-solution mechanism. The second is a process by which some ettringite crystals sinter together by a solid-solid reaction where crystals grow together and sinter [149].

The most convincing research also relates directly to the secondary ettringite issue. It has been observed that the transition zone at the aggregate and steel interface in concrete has a higher proportion of ettringite than elsewhere in the bulk matrix [225]. This finding supports the through solution mechanism of formation, since constituents must dissolve and diffuse towards the steel/aggregate surface where ettringite is precipitated. In another series of experiments Monteiro & Mehta [228] showed a distinct gradient in ettringite concentration in the interfacial zone between aggregate and paste. Much larger quantities of ettringite are present immediately next to the aggregate surface. They concluded that this could only be explained by a “through solution” mechanism and not by a “topochemical” or “solid-state” theory whereby compounds do not dissolve. The importance of the “transition” zone to secondary ettringite formation is discussed in detail in Section 4.2.

### 3.5 The Chemical Stability of Sulphoaluminates

#### 3.5.1 Stability in Solution

The earliest studies (1929, [181]) on the stability of ettringite showed that it is more stable in solutions of calcium sulphate and calcium hydroxide than in distilled water. On the other hand, monosulphate in solutions of calcium sulphate, sodium sulphate, calcium chloride and sodium chloride tend to change to the high sulphate (ettringite) form. Lerch concluded that only the high sulphate form of sulphoaluminate can be stable under the conditions expected in concrete.

The instability of the monosulphate form was noted by Kalousek [156]. The AFm phase is a metastable compound; this is also confirmed by research that shows monosulphoaluminate is metastable below 70°C [204 reported in 132]. Once monosulphate forms it is metastable but may persist for indefinite periods under the right conditions; its metastability dictates that it will finally convert to the trisulphate form (ettringite) — this is confirmed by other, more recent, research [163].
The formation of monosulphate requires nearly saturated solutions of both calcium hydroxide and gypsum. If excess sulphate is not present the monosulphate may persist for weeks but will finally convert to the stable trisulphate. The stability conditions in solution for monosulphate involve high CaO, low CaSO₄ and high temperature [152]. Mehta found that monosulphate hydrate forms in cement pastes along with ettringite "but persists only in contact with solutions of much lower sulphate concentration than required for stabilization of ettringite" [207].

At the normal temperatures experienced by concrete, Kelly found that ettringite is more stable than monosulphate or C₃A·₆H₂. Monosulphate readily forms at higher temperatures, however, which is due to its "greater crystallizability" as opposed to its higher stability [160].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>ettringite</td>
<td>1.0*10⁻⁴⁰</td>
</tr>
<tr>
<td>monosulphoaluminate</td>
<td>1.7*10⁻²₈</td>
</tr>
<tr>
<td>carboaluminate</td>
<td>1.4*10⁻３₀</td>
</tr>
<tr>
<td>chloroaluminate</td>
<td>1.0*10⁻３₀</td>
</tr>
<tr>
<td>calcite</td>
<td>8.7*10⁻０⁹</td>
</tr>
</tbody>
</table>

The table shows the solubility products for four major aluminates that are known to form in concrete. Calcite, a soluble compound, is included for comparison. Based upon this table, the following transitions can occur:

- calcium aluminate + calcium hydroxide + gypsum → ettringite
- monosulphoaluminate + gypsum → ettringite
- ettringite + NaCl → chloroaluminate
- monosulphate + CaCl₂ → ettringite + chloroaluminate
- monosulphate + CaCO₃ → ettringite + carboaluminate

This analysis may be an oversimplification of the issue. Hampson & Bailey [124] noted that ettringite does not exhibit a constant solubility product—it varies 5 orders of magnitude as the product of hydroxide and sulphate activity increases. This leads them to postulate that ettringite may lose its characteristic fibrous morphology at high pH and form a coherent coating over other particles. They note two possibly distinct forms of ettringite, depending upon the pH of the pore solution:

- at pH=11.5-11.8 — crystalline ettringite precipitates from solution
- at pH=12.5-12.8 — the result is a "topotactic" formation of a non-crystalline material that has a similar composition to ettringite.

The one special situation that the solubility product method does not predict is the formation of monosulphate from ettringite. Monosulphate has a solubility product at 25°C of 1.7*10⁻²₈, whereas ettringite has a solubility product of 1.1*10⁻⁴⁰. Normally, the most insoluble salt, ettringite, will preferentially be formed. However, when the sulphate in the pore solution is depleted, ettringite will convert to monosulphate. The extent of conversion depends entirely upon the amount of excess C₃A present after the initial formation of ettringite.

### 3.5.2 Stability and Temperature

For curing at 25°C ettringite is detectable by X-ray analysis after a few hours [302]. When hydration occurs at 60°C, however, ettringite X-ray peaks begin to form at 15 minutes and there is already appreciable ettringite at 6 hours. The ettringite crystals formed at the higher temperature are appreciably larger than those developed at 25°C [134].
At temperatures above 60°C, a different scenario develops. At approximately 70°C ettringite loses much of its water. For example, Daerr et al [79] note that the water content drops from 32 to 10 molecules at 70.5°C. Also, when water is lost between temperature of 70-85°C all ettringite compounds lose the molecular water in the channels and become amorphous [260]. Skoblinskaya et al agree; as ettringite loses water its structure remains intact only during the first-stage reduction from 30 to 18 water molecules. However, when water drops from 18 to 6 molecules during the second stage of desiccation the crystals become “roentgenoamorphous”. Withdrawal of the remaining 6 water molecules causes transverse rupture and the crystals disintegrate [290, 291].

There is a considerable diversity of research that quotes various temperatures at which ettringite decomposes. Abo-El-Enein et al [1] found that ettringite, when hydrated at 25°C, loses about 20 water molecules at 58°C in a dry atmosphere. If it is hydrated at 60°C, however, it loses 18 water molecules at 58°C; thus, formation at elevated temperature makes ettringite more thermally stable. Similarly, pressure also tends to stabilize ettringite against thermal decomposition—ettringite pellets were manufactured at two different pressures; the pellets made at the higher pressure were more stable when heated [2].

Some research has concentrated upon examination of ettringite decomposition under very severe conditions. Although in pure water ettringite is stable at 60°C at a pH of 11.2, at 100°C 2.25 moles of sulphate are split from the ettringite crystal, and monosulphate forms. If temperature remains at 100°C the monosulphate decomposes to gypsum after 21 days of boiling. At lower temperatures (30°C), monosulphate is unstable and decomposes partially to ettringite after 6 hours. At intermediate temperature (60°C) monosulphate enters into a solid solution with calcium aluminate hydrate in 6 hours, which decomposes to ettringite after a day [104]. Ghorab et al [106] report that the structure of ettringite is destroyed (a) at 18°C in a vacuum of 10⁻⁶ torr; (b) at 74°C under normal atmospheric pressure; and (c) at 82.5°C under wetted N₂. Re-storage at 90% r.h. leads to rehydration [106].

It has been postulated that up to approximately 70°C ettringite is the stable compound in cement and concrete, while above this temperature it is the monosulphate that is stable [ref. 143 notes the work of Mchedlov-Petrosyan [204]). There is some research, however that shows that ettringite can exist in equilibrium with its aqueous solution up to 90-93°C [277]. The apparent instability of ettringite at higher temperatures may be related to its higher solubility [106, 107].

Mehta reports that the short-prism type of ettringite found in the paste-matrix of concrete is stable at 65°C in a dry atmosphere, but decomposes partially at 93°C. In a moist environment, however, ettringite shows no significant decomposition at 93°C. However, if ettringite is exposed to saturated steam at 149°C it will decompose to the monosulphate. The fine-grained type of ettringite found in concretes and pastes is more thermally stable than the long slender needles of ettringite that form from dilute solution [214].

### 3.5.3 Post-Decomposition Behaviour

The combination of the SO₃ content of the cement and the heat-treatment régime determines the compounds that are present in a cement paste. Kalousek [157] tested pastes with 0.4 to 4% SO₃ which were cured at 24, 54 and 82°C. The pastes were put through a 19 hour heat-curing cycle, dried and analyzed. At 54°C curing, Kalousek noted that the most notable change over 24°C was the decrease in the amount of ettringite and increase in monosulphate. For curing at 82°C ettringite was absent except for specimens where SO₃ content was greater than 3%. There is an amount of “missing SO₃” which is larger in the 82°C cured specimen than in the 54°C specimen.

Kalousek proposed that heat curing results in an amount of SO₃ that is neither bound in the monosulphate nor in the ettringite. It was suggested that this missing ettringite becomes a “lattice sub-
stituent" in tobermorite (C-S-H) gel; the SO$_4^{2-}$ ions occupy sites of the SiO$_4^{4-}$ tetrahedrons. Other substitutions of ions such as Al$_2$O$_3$, Fe$_2$O$_3$, MgO and Cl$^-$ ions are well known and therefore there is no reason why SO$_4^{2-}$ cannot substitute also. Figure 3.3 shows the distribution of phases at the various treatment temperatures. As treatment temperature rises the amount of SO$_3$ missing (i.e. in "Phase X") increases. The presence of ettringite shifts to higher sulphate contents.

![Graph 1: 24 °C Treatment](image)

![Graph 2: 54 °C Treatment](image)

![Graph 3: 82 °C Treatment](image)

**Figure 3.3**

Effect of Curing Temperature on Sulphoaluminate Phases [data from ref. 157]

Type 30 cement. DTA analysis performed at age of 19 hours
In 1965 Richards [269] produced some interesting results that relate to the stability of ettringite. He soaked mortars in various sulphate solutions; the temperatures of the sulphate solutions ranged from 20 to 80°C. He found that soaking at temperatures greater than 40°C resulted in a dramatic reduction in expansions. Measurements were taken up to 24 months. Richards concluded that the expansion process that is normally very destructive does not take place above 20°C. It is unfortunate that he did not continue to measure expansions after specimens were cooled.

Odler [242] examined the hydration reactions of pastes containing cement with 0 to 20% C₃A, 3% SO₃, and a Blaine fineness of 3000 cm²/g. Curing temperatures ranged from 5 to 95°C. The researchers found that at 5°C gypsum was consumed within 3 days and the quantity of ettringite was large. At 25 and 50°C the conversion process from gypsum to ettringite was accelerated; both AFt and AFm phases were present at 28 days. At 75°C curing AFt was only present during the first few hours, while AFm was observed at all times up to 28 days. At 95°C no AFt was detected at all; AFm formed instead but disappeared after 3 days. Similar results were obtained for all of the cements examined. Odler concluded that as temperature rises there is an enhanced incorporation of Al³⁺, Fe³⁺ and SO₄²⁻ into the C-S-H lattice.

The disappearance of ettringite with elevated temperature was well documented by Chino & Kawamura [56]. Hardened cement pastes (w/c=0.5) were cured for 14 days at temperatures ranging from 20 to 90°C. Ettringite was determined by X-ray diffraction. As Figure 3.4 shows, the quantity of ettringite in the paste dramatically decreases at curing temperatures above approximately 70°C.

Stadelman [294] used differential thermal analysis to analyze the stability of ettringite content in hardened cement pastes when treated at temperatures ranging from 20 to 100°C. When ettringite

![Figure 3.4](image_url)

Figure 3.4
Variation in Ettringite Peak Intensity with Curing Temperature [data from ref. 56]
was treated at temperatures above 60°C it no longer appeared on DTA traces; instead, monosulphate appeared. During storage after treatment, ettringite peaks reformed which, Stadelman concluded, “must be seen as a cause of concrete damage”.

3.6 The Effect of Alkalis on Hydration and Formation of Ettringite

Alkalis are normally present in the clinker as the neutral sulphates Na₂SO₄, K₂SO₄ or the mixed salt (Na,K)₂SO₄ [71, 252]. These compounds are highly soluble. After contact with water the pore solution contains almost entirely Na, K and OH ions with “very low” concentrations of Ca, SO₄ and Cl. The pH of the pore solution is in the range 13-14, depending upon the alkali level. If no alkali is present then pH=12.5 [71].

Alkalis accelerate the hydration process through the alteration of the C₃A—CSH₂—CH system [105]. The main action of the alkalis is to increase ettringite solubility and decrease lime solubility [79]. This is confirmed by Wang et al [315] for example: The molarity of pore solution when low-alkali cements are used is approximately 0.2M with respect to alkalis; normal cements produce a molarity of greater than 0.7M. The pH in the pore solution might reach 12.9 within minutes and 13.7 or higher after 28 days. Gypsum does not affect this pH value. The OH⁻ concentration due to alkali is on the order of 15 times greater than the concentration of saturated calcium hydroxide solution. Therefore, the presence of alkalis decreases the solubility of CH and accelerates the formation of ettringite; these findings are supported by similar conclusions of Daerr [79]. Experiments also show that ettringite forms even at a pH of 13.3.

An alternative mechanism for ettringite formation in alkali solution is given by Chino & Kawamura [56]. They hypothesize that in the presence of NaOH, ettringite formation is suppressed because SO₄²⁻ is more stable in Na₂SO₄ than in ettringite. The retardation of ettringite formation results in an acceleration of early hydration of C₃A. Through the reaction of NaOH, ettringite is decomposed as:

\[
3\text{CaO-Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot31\text{H}_2\text{O} + 6\text{NaOH} \rightarrow 3\text{Na}_2\text{SO}_4 + 4\text{Ca(OH)}_2 + 2\text{Al(OH)}_3
\]

Way and Shayan [316] looked at the hydration of Portland cement in 0.5 and 1.0M sodium hydroxide solution. They found that the nature and appearance of all hydrates were the same as in water. The alkali did accelerate the time for depletion of sulphate ions by the formation of ettringite.

In alkaline solution at 30°C (0.08M NaOH), Wang et al [315] found that the stability of ettringite is the same as in water. However, at higher temperatures (60°C, 0.08M NaOH) ettringite partially decomposes to the low sulphate form. Both phases can exist for long exposure times under these conditions. Higher alkali concentrations (0.2 to 1.0M) decompose the ettringite very quickly, while the stability of monosulphate hydrate rises in the more concentrated alkaline solutions [104].

3.7 The Role of CO₂ and Carbonates

Grounds et al [122] reported research where samples of lab-manufactured ettringite were stored in sealed containers at 25-95°C and 100% relative humidity (over water). At all temperatures ettringite showed complete decomposition to other phases. The time of decomposition was 55 days for 25 and 50°C storage, and 15-20 days for 75 and 95°C storage. The decomposition was attributed to the action of very small quantities of CO₂ in the system. The decomposition products
were identified as (a) gypsum, (b) calcite, (c) aluminium hydroxide, and (d) water according to the equation:

\[ 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \rightarrow 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 3\text{CaCO}_3 + 2\text{Al(OH)}_3 + 23\text{H}_2\text{O} \]

Ghorab et al. [106] found that in real pastes and in the presence of CO\textsubscript{2}, ettringite decomposes to gypsum, bayerite and aragonite. Carbonation also produces a much more porous microstructure [106].

### 3.7.1 Formation of Thaumasite

Despite the fact that Grounds tested an “ideal” system, his research indicates the potential for carbon dioxide to alter ettringite. In practice, carbon dioxide has a role in the formation of “thaumasite” from ettringite. Both ettringite and thaumasite formation have been found to be the cause of damage to plaster [179].

It is postulated that the formation of thaumasite involves expansion similar to that due to the formation of ettringite [142, 173]. The formation of ettringite usually precedes that of thaumasite, but both compounds can exist together [68]. Both ettringite and thaumasite are produced more rapidly at cold ambient temperatures (0-10°C). Their chemical formulae are [74]:

- **Ettringite:** \[ \text{Ca}_6[\text{Al(OH)}_6]_2 \cdot 24\text{H}_2\text{O} \cdot [\text{SO}_4]_3 \cdot 2\text{H}_2\text{O} \]
- **Thaumasite:** \[ \text{Ca}_6[\text{Si(OH)}_6]_2 \cdot 24\text{H}_2\text{O} \cdot [\text{SO}_4]_2 \cdot [(\text{CO}_3)_2] \]

The similarity of the two chemical formulae reflects the fact that both thaumasite and ettringite are AFt phases with similar crystal structures (see Section 3.3) [203]. Hunter noted that thaumasite forms a solid-solution series with ettringite. At temperatures greater than 15°C ettringite probably forms first and then later converts to thaumasite [142].

Taylor [302] stated that the combination of sulphate attack and carbonation (which occurs often in practice) can result in the formation of thaumasite; this can cause severe softening or cracking. “It can easily be misidentified as ettringite”. Thaumasite’s formation requires a constant high relative humidity in a cold environment (4°C), an adequate supply of SO\textsubscript{4}\textsuperscript{2-} and CO\textsubscript{3}\textsuperscript{2-} and the presence of reactive aluminate. Thaumasite does not form directly, but requires ettringite to form first which acts as a nucleating agent. Whereas the quantity of ettringite formed is limited by the available Al\textsubscript{2}O\textsubscript{3}, the amount of thaumasite formed is only limited by the lime and silica contents, since alumina is not part of the compound. A continuous source of sulphate ions would allow thaumasite formation to effectively destroy a mortar or concrete through a softening reaction.

Ludwig & Mehr [193] examined deterioration of historical buildings. They found that at temperatures between 2 to 40°C, damage was due to ettringite formation. However, at later ages and at temperatures less than 20°C, ettringite decomposed to thaumasite in the presence of unreacted gypsum and calcite. No evidence was gathered that the formation of thaumasite caused expansion. Ettringite and thaumasite form a mixture, but do not participate in a solid solution.

Sylla [297] noted that thaumasite may have a role in influencing expansion after heat treatment. He stated that when conditions are right then both thaumasite and ettringite can form with time after heat treatment. For example: a paste sample was heat-treated at 80°C for 5 hours, then stored at 5°C with CO\textsubscript{2} present; analysis showed a mixture of ettringite and thaumasite present with a high proportion of thaumasite. Sylla believes that both thaumasite and ettringite formation after heat treatment can cause damage; the sulphate is supplied from where it is weakly bound to the calcium silicate hydrate during heat treatment.
3.7.2 Formation of Carboaluminates

The addition of limestone to cement, or the presence of limestone aggregate in concrete, can result in the formation of carboaluminates as early as 7 days after the start of hydration. In a system with Portland cement clinker, 2% gypsum and 6% limestone calcium carbonate reacts with C₃A to form calcium carboaluminate hydrate. There appears to be both a high and low form of carboaluminate, similar to a high and low form of sulfoaluminate. Although carboaluminates form, ettringite formation proceeds normally in the presence of limestone.

Klemm and Adams [163] outlined three functions that limestone fulfills when it is present in concrete: (1) it acts as a micro-filler, thus improving strength; it may also act as a nucleation agent to accelerate cement hydration; (2) carbonates can accelerate C₃S hydration and the carbonate can be incorporated into the C-S-H phase; (3) With fine limestone the principal interaction is to react with aluminates and ferrites to form calcium carboaluminate (ferrite) hydrates. This interaction can contribute as much as 10% to the compressive strength between 2 and 28 days.

The carboaluminates also form AFt and AFm phases. These are:

- **AFt**: C₃A·3CaCO₃·27H₂O → needles
- **AFm**: C₃A·CaCO₃·11H₂O → hexagonal plates

The AFt phase is much less stable than the AFm phase, and thus is unlikely to form in cement paste. When carbonate is present it slowly dissolves and will react with any monosulphate present to form the carboaluminate which is the more stable phase because it has a lower solubility product than monosulphate. The chemical formula is:

\[ 3\text{C}_3\text{A}·\text{CaSO}_4·12\text{H}_2\text{O} + 2\text{CaCO}_3 + 18\text{H}_2\text{O} \rightarrow 2\text{C}_3\text{A}·\text{CaCO}_3·11\text{H}_2\text{O} + \text{C}_3\text{A}·3\text{CaSO}_4·32\text{H}_2\text{O} \]

In other words, monosulphate decomposes in the presence of carbonate and water to form both a carboaluminate \textit{and ettringite}. Both the carboaluminate and the ettringite are very stable and can co-exist. This is a slow process; the presence of limestone (either in the aggregate or due to carbonation) can result in a later-age ettringite formation. The tests that were performed by Klemm and Adams with 5% limestone addition showed the start of carboaluminate formation at an age of 91 days. Note that the sulphate ion can also react with monocarboaluminate, as well as monosulphoaluminate, to form ettringite. The carbonate ion will not react directly with ettringite because the result would be more soluble (less stable) products.

Kuzel and Strohbauch [172] note that expansive damage can occur due to ettringite formation as a result of “carbonation reactions of the calcium aluminate hydrates crystallizing in the laminar mode”. Also, if CO₂ is present in an environment where pH is greater than 12, the C₄A·SO₃·aq groups in the interlayer of the monosulphate are displaced by CO₃²⁻ ions. This reaction leads to the formation of a hemi-carbonate (C₄A·½CO₂·aq) and gypsum. The gypsum then reacts with the unchanged fraction of monosulphate to form ettringite. In a strong alkaline medium the hemi-carbonate reacts as follows:

\[ \text{C}_4\text{A}·\frac{1}{2}\text{CO}_2·\text{aq} \rightarrow \text{monocarbonate} \rightarrow \text{CaCO}_3 + \text{Al(OH)}_3. \]

Although this process of reaction is explained differently, the formation of ettringite from the reaction between monosulphate and carbonate is essentially the same as proposed by Klemm and Adams [163].

Calcite has one other function. The reaction between C₃A and gypsum to form ettringite, and the conversion of ettringite to monosulphate are accelerated by the addition of CaCO₃. The calcite reacts with aluminate to produce carboaluminates. Under certain conditions all of ettringite, monosulphate and carboaluminate can co-exist. As well as carboaluminate, a solid solution of
hexagonal calcium aluminate hydrate, monocarboaluminate and sulphaaluminate hydrates may also exist [265].

3.8 Formation of Chloroaluminates

Richartz [270] stated that chloride can combine with all phases in a cement clinker. In solutions where the chloride concentrations are up to 10g Cl⁻ litre, C₃A and aluminoferrite can form Friedel’s salt, which has the formula: 3CaO·Al₂O₃·CaCl₂·10H₂O (a monochloroaluminate). At higher Cl⁻ concentrations, a tri-chloroaluminate phase that resembles ettringite can form; the formula is: 3CaO·Al₂O₃·CaCl₂·32H₂O.

If gypsum is also present, Richartz notes that at normal temperatures ettringite always forms first; the chloride containing compounds form after the gypsum is consumed. At elevated temperature (40-80°C) Friedel’s salt forms instead of either ettringite or the chloroaluminate phase, even when gypsum is present. Friedel’s salt is shown to be stable in water and in saturated CH up to 90°C.

This analysis [270] suggests that heat treatment may be beneficial for reinforced concrete where substantial amounts of chloride are present. Friedel’s salt is preferred over ettringite formation and therefore the chloride is tied up and unavailable for the corrosion reaction. Note, however, that if Friedel’s salt is present at 20°C, sulphate acts on it to form ettringite while the chloride goes into solution; this would be a slow process that could result in later expansions.

Richartz’ analysis is supported by Worthington et al [324]. They found that chloroaluminates do not form at the expense of ettringite, but do form preferentially over monosulphate. Ettringite may reappear due to the breakdown of monosulphate to form chloroaluminate. Since the amount of chloroaluminate formed is related to the alumina content, blended cements can form more than normal cements. Chloroaluminates appear to be stable; the trichloroaluminate is the more stable form at lower temperatures [283].

If Cl⁻ ions are present, chloroaluminates can form from the first stages of hydration. Chlorides promote the formation of a porous C-S-H. This effect subsequently promotes the penetration of magnesium ions (if present) into the hydration product and “conversion of C-S-H to the non-hydraulic M-S-H” may occur [102].

When exposed to seawater, Type I cements show both chloroaluminate and ettringite formation. At early ages these products deposit in the voids and exert little expansion [158]. If temperatures are low the presence of NaCl causes ettringite to decompose to form Friedel’s salt. At lower temperatures in a chloride environment the Cl ion can be incorporated into the ettringite structure; this results in a “less-expansive phase” [243-245]

3.9 Morphology of Ettringite

The controversy over whether ettringite forms by through-solution mechanism [220] or by topochemical means [222] has also resulted in two hypotheses concerning the morphology of ettringite in the hardened cement-paste matrix. Mehta [209] noted that ettringite has two types of morphology, depending upon the conditions under which it forms:

- **Type I:** are large lath-like crystals 10-100µm long and several µm thick. These form in solution under conditions of low hydroxyl ion concentration. These crystals are not expansive. These are the type of crystals that have been produced in numerous lab-based re-
search projects and of which thousands of scanning electron micrographs have been taken.

- Type II: are small rods 1–2 μm long and 0.1–0.2 μm thick. These form when the hydroxyl ion concentration is high (i.e. the normal situation for concrete). Ettringite formed with this structure can be a source of strength, or can cause disruption when, in a confined space, agglomerations of these crystals absorb water and expand. It is also possible to prepare this type of ettringite in the laboratory, but special techniques are required [216].

Mehta [207] notes that in concretes the calcium-sulphate hydrates form in a supersaturated environment. Under these circumstances the crystal structure of both monosulphate and ettringite are extremely fine-grained. The ettringite crystals are short prisms with a thickness:length ratio of 1:3.

This does not mean that the larger crystals do not form, because there is ample evidence of their occurrence in concrete. However, it is conjectured that Type I morphology only appears when sufficient space is available, such as in high w/c pastes, in large cavities, or during early hydration. In more restricted spaces, Type II ettringite occurs as “short prismatic crystals”; under these conditions ettringite appears to be able to form “anywhere and everywhere” in the system [213].

As will be shown below, the presence of the smaller “colloidal” size ettringite provides the cornerstone of a hypothesis concerning the expansion mechanism. Accordingly, in support of the Type II morphology, Mehta [205] noted that the presence of lime in Portland cement pastes and concretes affects the formation of ettringite such that it has a colloidal morphology, and does not form as long lath-like crystals. The colloidal nature of the ettringite results in the attraction of large numbers of water molecules which cause interparticle repulsion and expansion [213].

### 3.10 Mechanism of Expansion Associated with Ettringite Formation

As mentioned above, there is controversy surrounding the fundamental mechanisms associated with the formation of ettringite and subsequent expansion. Cohen [60] has categorized the hypotheses into two schools — crystal growth and swelling.

#### 3.10.1 Crystal Growth

In the “crystal growth” school expansion is caused by the formation of ettringite at the surface of reactant grains. The growth of this inner layer pushes other particles out and thus causes expansion. The mode of formation also appears to depend upon whether CH is present or not — if it is not present then crystal growth is topochemical, if CH is absent then ettringite forms from solution and does not produce expansion.

Research on sulfo-aluminate based expansive cements (Type K) [61] shows that expansion is caused by growth of ettringite crystals on the surface of expanding particles; a topochemical reaction between the particle and the surrounding solution is responsible. The magnitude of expansion does not depend upon the quantity of ettringite formed but on the size of crystals produced. A few long crystals at a small number of sites can produce large expansions and microcracks. Alternatively, formation of small crystals at a large number of sites can produce a network of smaller microcracks.

Chatterji and Jeffery [52] have hypothesized that expansion due to the presence of sulphates is caused by the solid state conversion of $\text{C}_4\text{AH}_13$ to monosulphate hydrate in the presence of CH. This hypothesis has been researched in detail by others. Mehta, for example, was not able to reproduce Chatterji’s results and could not detect the presence of $\text{C}_4\text{AH}_13$ [208]. It is now com-
monly held that expansion is due to the formation of ettringite and not monosulphate. Even if Chatterji's theory about monosulphate formation was correct, Mehta [207] has shown that monosulphate formation in a confined space should not result in expansion because the plate-like monosulphate crystals can orient themselves like "leaves of a book". On the other hand, ettringite crystals do not re-orient and therefore are more likely to be able to exert pressure.

The hypothesis that pressure can be exerted from individual crystals is contrary to the findings of a number of researchers. Dron et al [88] noted that ettringite's expansive forces can only develop in a confined space. A uniaxial force of only 1 MPa is sufficient to inhibit expansion in that direction; ettringite will then proceed to grow in another direction. The destructiveness of ettringite formation depends upon where in the matrix it forms. If it forms near an aggregate particle then destruction is maximum. If it forms near a cavity, then the cavity can act as an expansion chamber to relieve potential stress build-up.

Very recently, Ping & Beaudoin [256,257] postulated that formation of ettringite is by two processes, nucleation and crystal growth. The production of "crystallization pressures" requires a confined space in which the crystals grow. The lack of a confined space explains why ettringite growth does not cause pressures during early stages of hydration. Most of the ettringite may form before expansion occurs; it is only the formation in confined space that produces expansion. In fact, Beaudoin & Ping note that any solid product will produce crystallization pressure if:

- crystal growth is in a confined space
- the solubility product ratio is greater than 1.0 (i.e. the products are less soluble than the reactants)

3.10.2 Swelling

Cohen [62] summarizes the "swelling school" of thought: ettringite forms by a through-solution mechanism. In a saturated CH environment ettringite crystals are gel-like and colloidal in size. The high surface area results in adsorption of significant quantities of water and strong swelling pressures develop.

The theory was first proposed by Mehta [215,217]; the expansion mechanism for ettringite is similar to that of some clays which expand because of "polar oriented electrostatic attraction of water molecules". Small ettringite crystals of colloidal size, formed in an alkaline environment possess a negative surface charge. The high surface area combined with the negative charge result in an attraction for large quantities of water. Tests on disks of pure ettringite confirm the hypothesis; the disks adsorb a large quantity of water and large swelling strains occur. A check of the XRD pattern of the ettringite before and after swelling shows no substantial change.

Early fundamental research by Seligmann & Greening [285], as well as other research [295] tend to support Mehta. Seligman & Greening found that when C3A pastes hydrate they undergo large volume increases due to imbibition of large quantities of water. As an example, pastes were prepared with S/A mass ratios from 1/8 to 1.0. The water/cement ratio was 0.4 to provide just sufficient water for ettringite formation. Nevertheless, during soaking for 180 hours after casting, much larger quantities of water were taken up and the fresh pastes showed as much as 57% expansion. When sodium or potassium hydroxide was added, all reactions accelerated; there were no observable changes in the nature of the reaction products.

Sagrera's work [273] is also supportive. He mixed paste cylinders containing either calcium sulphate or sodium sulphate additions. Volume change was measured and the quantity of ettringite in the pastes was determined by X-ray diffraction. Figure 3.5 clearly shows the positive correlation that exists between ettringite content and % volume increase.
Figure 3.5
Correlation Between Volume Increase and Ettringite Content [data from ref. 273]

However, also note that in Figure 3.5 a significant amount of ettringite forms before there is any volume increase—i.e. there is an X-axis intercept that is greater than zero. Sagrega's results could accommodate both the swelling theory and the "crystal growth in confined space" theory as described by Ping & Beaudoin [256, 257].

Like many other observed processes that occur within concrete, there is undoubtedly no single mechanism that determines behaviour. Both mechanisms — swelling and crystal-growth — are active; environmental conditions at any particular time determine which, if any, is predominant.

Mather [199], in his discussion of Cohen's work [62], summarizes the issue from an engineering viewpoint. He argues that the details of the formation of ettringite are of less importance than the fundamental mechanism involved in the process. The fact that the morphology of ettringite is crystalline or not is "of minor importance". The important factor is that the products attempt to occupy a larger volume than is available for their formation. Mather quotes from ACI Committee 223 that "thermodynamics shows that there exists a very large amount of free energy, about 55 kcal/mol (formed from C₃A) which equals about 169,000 ft-lb of work". Thus, ettringite formation in a confined space is capable of producing very high forces. Clearly, these forces cannot develop unless there is a rigid framework to resist the forces.

Mather continues: the mechanism of development of expansive forces involves the alteration, in situ, of a quantity of aluminate reactant to form ettringite "by a process that delivers water and other reactants in solution to the reaction site, and leaves elsewhere in the structure some space formerly occupied by solution that is no longer filled with solution". From a review of crystal growth theory, Mather concludes that "when you put more than one unit volume of anything in a restrained three-dimensional space having, initially, a size of one unit volume something has to
give; either the quantity added must reduce itself in amount (some leaks out) or in volume (it is compressed) or the space enlarges either elastically or inelastically without rupture or it cracks". The most important fact is that the volume that ettringite forms per unit volume of C₃A used is 8:1; "the fact that the ettringite is crystalline or colloidal is irrelevant".

3.11 Mechanism of Secondary Ettringite Formation

Ettringite needs sulphate to be in solution to form. Its formation during sulphate attack is easily explained, since sulphate ions penetrate the concrete microstructure from outside. However, in

Figure 3.6
Formation of Ettringite from Sulphates Supplied by C-S-H
DTA results taken directly from Odler [240] and annotated
In this report we are considering mechanisms by which ettringite forms at later ages without assistance from outside sources.

The key to explaining this mechanism lies in the research of Lerch [180, 181] who found that during hydration some sulphate goes "missing" and form "Phase X" (Fig. 3.3). By 1980, these ideas had been clarified by Odler [240]: Odler examined the bonding of sulphate within C₃S pastes in order to confirm the initial findings of Copeland et al [72] that C-S-H can bind and then release sulphates. Odler's DTA results are summarized in Figure 3.6. An alite cement with 2.5% gypsum was hydrated for 28 days, ground to cement fineness and then blended with C₃A in a molar ratio C₃A/CaSO₄=1:3. The new cement was mixed with additional water to form a paste and allowed to hydrate. DTA and X-ray diffraction analyses were performed at various ages after drying at 35°C. The experiment was performed for alite cements with various sulphate additions and similar results to those shown in Figure 3.6 were obtained. X-ray diffraction analysis confirmed the DTA results.

The formation of the ettringite peak during the second hydration period and the absence of a gypsum peak after the start of hydration confirm that the sulphate is bound within the C-S-H structure. The "gypsum is bound by the C₃S hydration products in a way that makes it undetectable by the [DTA and X-ray] methods employed". The maximum amount of bound gypsum corresponds to 9.8 g SO₃ for 100 g of C₃S.

Another test showed that the sulphate in the C-S-H is readily extracted by saturated calcium hydroxide solution. Thus, when a source of aluminate is added to the ground paste containing C-S-H with bound gypsum, the ettringite peak quickly forms and reaches its final intensity within 3 hours after hydration.

Lachowski's findings are in support of Odler [174]. He examined the composition of C-S-H for pastes hydrated up to 900 days and concluded that over time SO₄²⁻ ions leave the C-S-H as the pastes age. Most of this loss, however, occurs during the first 28 days.

In Neck's research [237], concrete was manufactured with 400 kg/m³ of PZ55 high-early-strength German cement, at a w/c=0.36. Strength tests at 7 days gave 60-70 MPa and 70-80 MPa at 28 days. Behaviour after 2 heat treatments was compared: In treatment "A" there was no pre-cure, a temperature rise to 80°C at 60°C/hour and 80°C was held for 4 hours; in treatment "B", 3 hours pre-cure was used followed by a 20°C/hr rise to 65°C, which was held for 2 hours. For treatment A Neck postulated that some of the calcium sulphate remains mobile and is available for secondary phase formation when moisture is introduced. Free sulphate is a requirement for the expansion process, while moisture must be present to dissolve and transport the sulphate. Also, "crevices and disturbances" must exist for pathways for water and transport of ions. These also provide space for crystallization of the secondary phases.

Wickey et al [319,320] summarize the entire process nicely. During heat treatment the thermal decomposition of "primary" ettringite results in an increase of sulphate ion in solution and a decrease in OH⁻ ion concentration. Figure 3.7 shows the sulphate ion concentrations in the pore solution immediately after heat treatment for pastes with various S/A ratios and alkali contents. On the other hand, after heat treatment the pore solution changes with time. Figure 3.8 shows that the SO₄²⁻ concentration reduces steadily over 90 days for both a 60°C treated and 90°C treated paste.

Wickey et al propose that during heat treatment the ettringite formed during early stages of hydration is decomposed. The process is accelerated by alkalis. In the temperature range 50-80°C the reversible formula is:
Figure 3.7
Changes of Sulphate Ion Concentration with Heat Treatment
S/A = SO$_3$/Al$_2$O$_3$ Ratio; ALK = % equiv. alkali (data from ref. 319)

Figure 3.8
Change in SO$_4$ and OH Ion Concentration During Storage
(data from ref. 320)
At temperatures greater than 70°C monosulphate also decomposes according to the reversible formula:

\[
3\text{CaO-Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O} + 4\text{NaOH} \xrightarrow{\text{50–80°C}} 3\text{CaO-Al}_2\text{O}_3\cdot12\text{H}_2\text{O} + 2\text{Na}_2\text{SO}_4 + 2\text{Ca(OH)}_2 + 20\text{H}_2\text{O}
\]

3.12 Comment

The AFm phase in Concrete is very complex both chemically and morphologically. One of its astonishing features is the wide variety of ions that can substitute in ettringite for Al and sulphate ions, while the basic crystal morphology remains the same. The complexity makes ettringite very useful for a wide variety of industrial applications, but it also causes problems when one wishes to determine the influence of the trisulphate phase on the engineering properties of concrete.

From an engineering viewpoint one important research finding is that ettringite does not appear to be stable in concrete at temperatures above approximately 60-70°C. When pastes, mortars or concretes are cured at elevated temperature ettringite disappears and some of the sulphate goes “missing”. Various ideas have been put forward, but the most accepted view is that at elevated temperature sulphate can easily be incorporated into the C-S-H gel structure. Various solid solutions may form. Further transformation of ettringite to monosulphate may also play a key role in this regard.

Whatever the exact mechanism, it appears that a sufficiently high heat treatment results in the sulphate being unusually bound. The bond is such as to allow a later slow release of sulphate ion into the pore solution and combination with aluminates to produce ettringite. It also appears that other compounds such as carbonates, chlorides and carboaluminates may influence the formation of expansive compounds at later ages.

The mechanism by which ettringite produces stress and strain is also not precisely known. Mather’s viewpoint is therefore preferred; from the practical viewpoint we are interested in knowing under what conditions compounds form which try to occupy more space than is available within the pore structure of the material.
Chapter 4
Secondary Ettringite Deposition

4.1 The Importance of Porosity to Ettringite Formation and Expansion

Post-mortem studies of deteriorated concretes tell us a considerable amount about how ettringite and other crystalline materials form. Many studies show crystalline deposits within the capillary and air-entrained pore structure.

For example, Gillott and Ritchie [112] examined cement pastes that were 50-70 years old. They observed various crystals forming in the small voids in the pastes. These were identified as: (1) thin plates, frequently extending from one side of the void to the other, which were identified as CH crystals; (2) radiating clusters of needles or spherulites; these were identified as ettringite crystals.

Murat [233] examined the fracture surface of asbestos fibre-reinforced cement paste used to manufacture hot-pressed pasteboard. He discovered a number of large voids that were filled with “flower-like” crystallization product. Murat noted that calcium sulphate becomes concentrated in voids; “ettringite grows in flowers from a seed”.

Specimens that had undergone freeze/thaw attack show crystals of portlandite and ettringite in the air voids [236]. It was hypothesized that a reduction in the lime concentration in solution (which can be brought about by a number of different effects) results in an increase in the solubility of hydrated calcium aluminates. The freezing action in the pore structure results in pore solution being expelled into the voids where conditions are right for ettringite to form. Formation of ettringite in the pores does not result in expansive pressures.

St. John [293] noted that ettringite crystals are often found in the pores and cracks of concrete that has deteriorated. These crystals are deposited in the voids as a result of movement of fluids through the pore structure. The presence of ettringite in this form does not appear to be harmful to the concrete. However, there are “sub-microscopic particles of sulphoaluminates dispersed through the concrete” that may be “remobilized into solution” as the concrete deteriorates. Recrystallization can then occur “as visible needles at the nearest interface”. This phenomenon has been observed even in young concretes that have cracked due to overstress and have fluid flowing through the pore structure.

Observations of ettringite in the larger voids and cracks, including air-entraining voids, appear commonplace. At the same time, it seems that such formations are not directly responsible for “secondary ettringite” attack. It may be just the reverse: ettringite within these spaces may be indicative of a process that might have led to expansion and cracking, but which was relieved through the transport of the reactants to “free space” where the products form in a stress-free environment. Conversely, micro-porosity, concentration of key compounds, microcracks and a weakened microstructure around the paste/aggregate and paste/steel interface appear to be nucleation sites where secondary ettringite can grow and produce damage; this is the subject of the next section.

4.2 The Importance of the Aggregate/Paste and Steel/Paste Interface

At the heart of the issue with respect to the effects of secondary ettringite formation is the aggregate/paste-matrix interface, normally called the “transition zone”. Most petrographic examina-
tions have shown that if one wishes to find ettringite in a deteriorated concrete, the first place one should look is at the transition zone. This section will explain the reasons for this.

A macroscopic indication of the existence of the transition zone in some concretes can be obtained simply by visual observation. For example, Hoshino [140] observed that the porosity of paste near the lower boundary of coarse aggregate is higher than elsewhere in the matrix. At the lower layer the boundary was “comparatively whitish” and contained a large number of CH crystals. At the upper boundary the amount of CH and the crystal size was much smaller. Using a more sophisticated procedure, Kayyali [159] noted that if one compares the porosity of concrete, aggregate and cement paste by mercury porosimetry, one finds a discrepancy in the porosities. This discrepancy indicates the existence of a higher porosity, or “interfacial layer” at the surface of the aggregates.

The early fundamental work of Hadley [123] and, later, Barnes [17] produced a clear picture of the transition zone which has since been substantiated by a large volume of research. In his PhD thesis, Hadley outlined the steps in the formation of the paste/aggregate interface

- after consolidation of the concrete there exists a “considerable volume” of water-filled space immediately around the aggregate
- Very quickly a film of lime, 1/4µm thick deposits directly onto the aggregate surfaces. This lime is “perfectly oriented”, with the c-axes normal to the aggregate surface
- a layer of C-S-H deposits on top of the lime film
- after 4-8 hours “large and randomly-oriented” lime crystals form in the “interfacial void”. These crystals grow to encapsulate hydrating cement grains.
- after 1-3 days “ettringite needles” and “booklets” of “large platy hexagonal crystals” also deposit in the interfacial region. The “booklets” were confirmed not to be lime or monosulphate; instead, Hadley postulates that they are “a complex solid solution of Ca, SiO2, Al2O3 and sulphur.

Observation of fracture surfaces shows that fracture occurs mainly through the interlayer void space. As the concrete ages, fracture occurs through the lime portion of the interfacial film, or through aggregate particles if weak cleavage planes are evident. Fracture never occurs at the true paste-aggregate interface. Hadley noted that some degree of orientation of CH occurs in the region up to 150-200µm from the surface. Figures 4.1a and 4.1b show Hadley’s schematic of the interfacial region at 30 minutes and 3 days after the start of hydration.

The research of Monteiro and co-workers [225, 226, 229, 84] has provided valuable information about the transition zone. The aggregate/paste-matrix interface is a weak zone in the concrete with higher porosity than the bulk matrix [226]. Calcium hydroxide is deposited with preferred orientation in the region within 30µm from the surface. Both coarse aggregate and sand grains show a calcium hydroxide coating with the c-axis perpendicular to the aggregate surface. The ettringite content in the transition zone is approximately 2.5 times that in the bulk matrix at 1µm from the surface and only reaches the bulk matrix levels 20µm from the surface. The thickness of the transition zone is larger for larger aggregates.

Monteiro et al [225] have examined the transition zone at the steel-paste interface. This zone is very similar to that occurring at the paste-aggregate interface. The CH that deposits in the transition zone has preferred orientation; further tests show that pronounced orientation still exists after 420 days in a 50µm region near the interface. The transition zone has high porosity and the crystals are larger than in the bulk matrix. There is a higher concentration of ettringite crystals in the transition zone, but the ettringite crystals have no preferential orientation (Figure 4.2). The dominant effect as aging occurs is the densification of structure behind the CH film. This densification
Figure 4.1
The Paste/Aggregate Interface at 30 Minutes and 3 Days
(drawings scanned from Hadley [123] and annotated)
process is assisted by the presence of silica fume. The steel/paste transition zone is not significantly different than the aggregate/paste transition zone.

In 1988 the issue of whether CH was truly orientated in the transition zone was clarified. Detwiler and Monteiro [84] addressed the criticism that the standard X-ray diffraction technique to determine CH orientation near the aggregate interface was inaccurate; the argument was that during analysis crystals which are not oriented with either a 0001 or 10T1 plane are missed. Instead, the researchers used a pole-figure goniometer which eliminates this presumed bias. They found essentially the same results as standard X-ray analysis—namely, that CH is oriented near aggregate surfaces.

The type of aggregate at the interface, however, does have an important role to play. The transition zone near carbonate aggregate is different than that for other aggregates, because a “basic calcium carbonate hydrate” forms which substitutes for the large and highly oriented CH crystals [229]. The carbonate-hydrate has smaller crystals and therefore there is a strengthening of the transition zone. The formation of this material occurred with both opc and C3S pastes; carboaluminates in the transition zone do not appear, therefore, to be the reason for the increase in mechanical strength.

The superiority of limestone aggregate in this regard is confirmed by Saito and Kawamura [275]. They examined the transition zone for ordinary cement pastes cast against two types of polished aggregate—limestone and granite. Fly ash and slag paste/aggregate interfaces were also examined. The researchers found that both ash and slag substantially reduce the formation of CH in the interfacial zone, but their analysis of plain pastes at an age of 36 days also showed some inter-

Figure 4.2
Variation in Ettringite Peak Intensity from Interface (data from ref. 225)
Figure 4.3
Compounds and Orientation in the Transition Zone — Limestone and Granite Aggregate
(data from ref. 275)
esting results (Figures 4.3). The interface normally extends from 50 to 100μm into the matrix. Ettringite and/or monosulphate exist in high proportions very close to the aggregate surface, but the quantity drops off rapidly and no X-ray peaks for either compound were observed further than 5-10μm from the surface. Both types of aggregate/paste interfaces showed similar results except for the significant finding that carboaluminates appear also to preferentially form near the limestone/paste interface (see Figure 4.3). In other tests it was found that the presence of fly ash and slag resulted in an increase of carboaluminate in the interfacial zone.

Larbi & Bijen [176] report recent results which further help to establish that calcium hydroxide orientation occurs. The orientation was revealed through an Orientation index which, if crystals are not oriented should be unity. Figure 4.4 shows test results from X-ray analysis near a paste-polypropylene interface; polypropylene was used to simulate a flat aggregate surface. The orientation index, and thus orientation, is maximum at the interface; some degree of orientation occurs up to 80μm from the aggregate surface. The introduction of fly ash has a pronounced effect in reducing the thickness of the transition zone from 60μm to 15μm at one month. As shown in Figure 4.4, the degree of orientation of calcium hydroxide is also significantly affected.

Figure 4.4 also illustrates the beneficial effects of fly ash; CH orientation produces weak planes: if orientation can be reduced then the transition zone is strengthened. Saito & Kawamura (above) noted similar improvements [275]. The use of pozzolanas is one method to improve the transition zone. Goldman & Bentur [113], for example, illustrated the beneficial effects of silica fume. The transition zone at the aggregate/matrix interface is a highly porous region. The solids contained in this zone have a heterogeneous microstructure. A “rim” of calcium hydroxide is frequently observed in contact with the aggregate surface. The “porous pockets” that are interspersed throughout the region contain a needle-like material that is “probably ettringite”. The interface region is shown in the first two drawings of Figure 4.5. When silica fume is present the transition zone is

![Figure 4.4](orientation_of Calcium Hydroxide Crystals, Age = 28 Days)

**Figure 4.4**
Orientation of Calcium Hydroxide Crystals in the Transition Zone (data from ref. 176)
Fresh Concrete without Fume

Filling of transition zone with Ca(OH)$_2$, C-S-H, and ettringite. Note porous pockets, some filled with ett

Fresh Concrete with fine silica fume particles

Transition zone in mature fume concrete

Figure 4.5

Schematic of Changes in the Transition Zone With and Without Silica Fume
(drawn scanned from ref. 113 and annotated)

entirely altered (see third and fourth drawings of Figure 4.5). The interface region is lower in porosity, is more homogeneous, and there are no porous pockets or CH rim around the aggregate.

Zimbelmann [327] suggested a method by which the aggregate/paste and steel/paste interface can be improved directly. In one series of tests, aggregate is coated with a normal commercial washing agent. The effect is to make the transition zone thinner. Zimbelmann found that the contact zone reduced from its normal 2-3µm to 0.5-1µm. This resulted in an increase in bond strength of 100-180%. In another series of experiments aggregate surfaces were coated with a suspension of pumice, detergent and water glass (sodium silicate); the objective was to replace the contact layer of CH with a layer of calcium silicates. Theoretically there should be a high "physical affinity" between the silicate contact layer and the aggregate and between the silicate contact layer and the hydrates. Tests showed that this method increased the bond strength by 200-270% at 100 days, and in some cases the bond strength exceeded the tensile strength of the hardened cement paste.
4.3 Comment

There is little doubt that the transition zone in normally-cast concrete is the weak link. It has higher porosity than the bulk paste, it has oriented CH crystals, it contains other crystals of unknown origin, and it is a region where sulphates are concentrated.

It is also a region where materials of distinctly different properties meet. The most important difference is the thermal expansion coefficient between aggregate and hardened cement paste. One intuitively expects, therefore, that if heat-treatment of concrete is going to produce damage, the damage is going to occur at the transition zone — between aggregate and paste (including both coarse and fine aggregate) and between steel and paste.

Given the properties of the transition zone, it is therefore not at all surprising that Heinz & Ludwig [132] conclude that for mortars showing substantial expansion due to secondary ettringite formation, SEM indicates that ettringite forms at the contact zone between paste and aggregate and that this is the “origin of the degradation”.
Expansion tests were performed on mortars manufactured with a typical German high-early-strength cement (with 4.0% SO₃) and a sulphate resistant cement. The heat-curing temperature varied from 60-100°C with a duration from 12 to 72 hours. Expansion tests were performed in accordance with DIN1164 and strains were measured to an age of 300 days. Mortar bars were 40x40x160mm bars made with a water/cement=0.5 and cement/sand=0.33.

The experiments indicated no significant late expansions occurred for curing temperatures less than 80°C, regardless of the period of heating. For treatments above 80°C expansions started after soaking in water for 70-80 days. Expansion was usually complete after 130 days soaking, except for the mortar cured at 90°C for 18 hours; this specimen showed continuously increasing expansion over the period 70 to 300 days.

In a second series of experiments specimens were subjected to a 1 day delay period followed by 1.5 days at 80°C and then a 6 hour temperature rise to 100°C; cooling followed immediately the specimens reached the maximum temperature. Figure 5.1 shows the expansion of bars manufactured with various blends of sulphate-resistant (SR) and high-early-strength (HES) cements.

Blends which contained more than 25% HES cement showed substantial expansions, again starting after about 70 days after the start of soaking. In all cases, expansions were accompanied by large reductions in resonant frequencies that were measured concomitant with deformation.

In a third series of tests the effect of repeated heat treatments was examined using the susceptible PZ55 cement. Set I specimens were heat treated at an early age while Set II specimens were not. Set I showed accelerating expansions after 50 days of soaking; this expansion (approx. 1.2%)
was finished after about 330 days. During this time, Set II specimens showed no appreciable expansion. At 330 days Set I specimens were subjected to a second heat-treatment and Set II specimens were given their first heat-treatment. Approximately 40 to 50 days after the treatment at 330 days Set I specimens started expanding even more and reached a total expansion of 2.5% at about 500 days. Set II specimens also started expanding about the same time (380 days) and reached a maximum expansion of about 1.7%, 200 days after their first heat-treatment occurred at an age of 330 days. The heat treatment appears to be a crucial component of subsequent expansion. Furthermore, it appears that the time at which the heat-treatment is applied is not very important; if anything, expansions are larger when the heat-treatment is delayed.

A fourth series of experiments examined the effect of pozzolans on the expansion mechanism. Various cement/pozzolan blends (containing the same amount of SO\textsubscript{3} as the PZ55 cement) were used to prepare mortars; these mortars were tested as above. It was found that the pozzolan substantially reduced expansions:

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% pozzolan: 100% PZ55 HES cement</td>
<td>1.00%</td>
</tr>
<tr>
<td>15% trass: 85% HES cement</td>
<td>0.70%</td>
</tr>
<tr>
<td>15% ash: 85% HES cement</td>
<td>0.15%</td>
</tr>
<tr>
<td>30% trass: 70% HES cement</td>
<td>0.05%</td>
</tr>
<tr>
<td>30% ash: 70% HES cement</td>
<td>0.02%</td>
</tr>
</tbody>
</table>

The authors suggest that the expansions are due to the formation of stable ettringite with time, derived from the monosulphate and solid solutions which contain tetracalcium aluminate hydrate. X-ray analysis clearly shows the development with time of the ettringite X-ray peak in the heat-cured sample, but not in the sample continuously cured at 20°C. Where calcium carbonate is present or carbonation is significant, Ghorab proposes that these can increase the damage caused by the gradual transformation to ettringite.

### 5.2 1984 — Research Institute of the Cement Industry [268]

Test disks of cement paste with dimensions 50 mm diameter x 10 mm thick were manufactured with various cements. Normal consistency was used. After various delay periods, specimens were heated over water at 100°C for 2 hours. The cements used had a C\textsubscript{3}A content of either 7.0 or 13.1%, 3% SO\textsubscript{3}, and 3500 cm\textsuperscript{2}/g Blaine. In some cements C\textsubscript{3}A activity was enhanced by adding K\textsubscript{2}O. Furthermore, the sulphate type that was used was varied—either gypsum or 1:1 anhydrite:hemihydrate.

Figure 5.2 shows the expansions of the disks measured at a constant time after the start of exposure. Clearly, expansion increases as the delay period decreases. Expansion was the largest at the lower C\textsubscript{3}A content of 7.0%. The addition of potassium oxide did not have a substantial effect on the results. In a parallel series of tests which used a 3 hour pre-storage, low expansions were also observed and were independent of the other parameters. It appears that the extent of prestorage is the critical factor which governs whether expansion will take place.

In a second series of tests the behaviour of concrete made from cements with higher SO\textsubscript{3} contents was examined. Concrete prisms, 4x4x16 cm, w/c=0.38, were manufactured with one of two clinkers in which sulphate was added to give either a 4% or an 8% SO\textsubscript{3} content. After a delay period of either 0 or 3 hours, specimens were heat treated at 40 or 80°C and a relative humidity of 60 or 95% for a period of 2 hours. After cooling, specimens were stored in water for 3 years at either 5 or 40°C.
Figure 5.2
Expansion of Paste Disks After Heat Treatment (data from ref. 268)
Note that if expansion was >12 mm/m (1.2%) cracks were observed

Table 5.1
Effect of Heat Treatment on Cracking and Phase Formation (data from ref. 268)

<table>
<thead>
<tr>
<th>Clinker</th>
<th>Pre-Storage (hrs)</th>
<th>SO\textsubscript{3} % by mass</th>
<th>Heat Treatment Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>40°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60%</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>4</td>
<td>![Gray Cell]</td>
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</table>

Dark Shading – designates strong crack formation accompanied by obvious new "phase formation"
Light Shading – designates slight crack formation with "insignificant" new phase formation
No Shading – indicates no substantial visual changes to prisms during 3 years storage

The qualitative results are presented in Table 5.1. Heat treatment at 40°C did not result in significant cracking for any combination of parameters, except for the very high sulphate cements which were not allowed a prestorage period. In most cases, heat treatment at 80°C led to cracking
and new phase formation. The 3 hour delay period had an important effect on subsequent behaviour.

5.3 1987 — Heinz and Ludwig [132]

This paper reports on continuation of experiments started by Ghorab et al [106]. Again, experiments were performed on mortar prisms in accordance with German specification DIN 1164. The high early strength cement had 12% C₃A and 3.8% SO₃ (denoted PZ55 cement).

In series I experiments mortar bars were heat-treated in the moulds after a delay of 2 hours. The treatment temperature varied from 20-100°C. The duration of heating was controlled in order that all samples had the equivalent treatment of 72 hours at 20°C. Bars were heat-treated in a water bath. After cooling, specimens were stored at 20°C in water during which time, length, weight, and resonant frequency measurements were taken. Measurements were taken to 1000 days of soaking.

Figure 5.3 shows the expansion, increase in weight and reduction in resonant frequency that occurred in the prisms that were heat-treated at different temperatures. There is clear indication that large expansions can occur if specimens are treated at temperatures above 75°C (all specimens treated at temperatures below 75°C [not shown] showed no significant changes with time of soaking). There is some indication that the 75°C cured prisms could expand significantly at ages greater than 1000 days (note that the rate of expansion starts to increase after 1 year) — also note the abrupt change in resonant frequency and increase in weight of the 75°C samples at 800 days.

Figure 5.4 shows that a positive correlation exists between weight gain and expansion after 28 days. This correlation is consistent with Mehta's hypothesis [205] that expansion due to ettringite formation is the result of imbibition of water and swelling of ettringite clusters. Figure 5.5 is a scattergram of expansion vs. change in resonant frequency; the correlation is not as good; the changes in resonant frequency, however, could be related to microcracking within the mortar as a result of expansive stresses.

X-ray analysis of specimens immediately after heat-treatment indicated that the amount of ettringite decreased as treatment temperature increased. Immediately after a 70°C treatment X-ray peaks corresponding to the monosulphate (AFm) phase were observed and, as treatment temperature increased, became the only sulphoaluminate present.

Heinz and Ludwig postulate that as treatment temperature increases the aluminates and sulphates form hydrates that have decreased definition. Most significantly, both the aluminates and sulphates are better incorporated into the C-S-H structure. Thus, at high temperatures ettringite decomposes, not necessarily to monosulphate, but so that the sulphates and aluminates are incorporated into the C-S-H structure.

The sulphate contained in the C-S-H apparently becomes mobile with time, because after 3 years storage the samples treated at 80-100°C contain "practically nothing but ettringite as calcium alumininate sulphate hydrate". In comparison, a sample stored continuously at 20°C shows both AFt and AFm phases.

In Series II experiments Heinz and Ludwig examined the influence of the S/A molar ratio on performance during soaking. In these tests anhydrite was added to the PZ55 cement to produce SO₃ contents within the range 2-8.6%; thus, the S/A ratio varied between 0.44 and 2.1. All bars were heat treated at 90°C for 12 hours in order to examine behaviour after a pretreatment period that is known to produce damage; a 2 hour delay period preceded the heat treatment.
Figure 5.3
Changes in Expansion, Weight & Resonant Frequency with Storage (data from ref. 132)
Figure 5.4
Correlation Between Expansion & Weight Gain (data from ref. 132)

Figure 5.5
Correlation Between Expansion and Resonant Frequency (data from ref. 132)
The expansion results are summarized in Figure 5.6. The figure clearly shows that if $S/A$ is less than 0.66 there is no expansion and no indication that expansion might occur after 1000 days. At an $S/A = 0.67$ there is a slight indication that expansion has started after about 800 days. Above $S/A = 0.67$, however, large expansions of bars occur. Furthermore, at intermediate values of $S/A$ (values that are entirely practical for Canadian cements) the rate of expansion can be dormant for as much as 1 year and then "suddenly" accelerate. At the very high $S/A$ ratios (1.5 and 2.1) the rate of expansion is appreciable from the start of storage and reaches 0.6% at 500 days.

It is important to note that times to the start of expansion are dependent upon the size of specimen. In a parallel series of experiments, Heinz and Ludwig noted that a change in specimen geometry from 40x40x160mm prisms to 10x40x160mm prisms produced expansions much earlier.

In Series III experiments the effect of relative humidity of storage was examined. The researchers found that below 95% rh no expansion or reduction in resonant frequency occurred. However, if specimens were stored at 60% relative humidity for an extended period (120 days) and then placed in a saturated atmosphere, the subsequent damaging reaction and expansion was intensified (Figure 5.7).

Series IV experiments looked at the effect of water/cement ratio and air-entrainment on the expansion process (Figure 5.8). A finding significant to the Canadian environment was that air-entrainment suppresses expansion. At the same time other experiments showed that freeze/thaw cycles magnify the problem; microcracks occur during f/t cycling which provide sites for formation of ettringite.
Figure 5.7
Effect of Humidity Change on Expansion (data from ref. 132)
2 hr. prestorage, 12 hr. treatment at 90°C, PZ55 HES mortar bars
5.4 1988 — Sylla [297]

Sylla reported upon European experience with secondary ettringite formation. As temperature rises in concrete the reactivity and speed of dissolution of C₃A increases, while at the same time the available sulphate in solution decreases. Therefore, there is an increased tendency to form monosulphate rather than ettringite. The importance of the treatment temperature and heat-treatment period on the quantity of ettringite present are clearly shown in Figure 5.9. Results are reported from pastes made with two cements: both cements had approximately the same sulphate content, but cement B had 12.1% C₃A. Cement A had 8.7% C₃A. The extra aluminate in cement B results in monosulphate forming in some pastes when treated at 60 and 80°C. The high C₃A cement also shows a more rapid reduction in ettringite content.

Sylla notes that the formation of monosulphate alone does not account for all the sulphate released when ettringite disappears. He postulates that the predominant portion of sulphate is “increasingly attached” to the C-S-H at high temperatures. In fact, this hypothesis is confirmed by parallel “microfluorescence” and thermal analysis studies. The results given in Figure 5.9 are for pastes that had no delay period. Sylla notes that for tests performed with a delay of 3 hours the ettringite formed during the delay period remained, even after 5 hours of treatment at 80°C.

Sylla also performed experiments to determine whether new phases form during storage after heat treatment. Paste specimens were stored at 20°C and 100% relative humidity after 5 hours heat-treatment at 40, 60 and 80°C. There was no delay time. Results are given in Figure 5.10.

For 40 and 60°C treatment there are no large changes in ettringite content as soaking time proceeds; In fact, for cement B ettringite content decreases with soaking time. After an 80°C treatment, however, there is a very large increase in ettringite during the first 28 days of soaking and a
Figure 5.9
Variation in X-Ray Peak Intensity with Curing Temperature (data from ref. 297)
small increase thereafter. After 56 days soaking, all ettringite peak heights are the same value for a given cement. Note also that for cement B the monosulphate content also increased with time for all specimens.

No cracking was observed in the pastes and Sylla hypothesizes that the newly formed ettringite is finely distributed over the entire sample. If microcracks were present, then transport processes may result in large local accumulations of ettringite, with subsequent destruction of a longer period.

5.5 1989 — Heinz, Ludwig & Rudiger [133]

In this paper the authors summarize the findings of a number of previous publications [125, 157, 159, 160, 161].
Mortars or concrete prisms were cast and heat-treated in water at temperatures between 50 and 100°C. Various heat-treatment temperatures and régimes were used, with all régimes designed to give the same 3-day strength for all specimens. A wide variety of cements were tested, including those with slag, fly ash, fume and limestone. Storage after treatment was normally in water at 20°C, but other storage media were also tried.

In general, it was found that to avoid damage the maximum treatment temperature should be kept to less than 70°C. There is no clear indication of the extent of delay period required; prestorage (delay) for 1 day to 1 year prior to heat treatment may lead to more damage because the structural matrix is stiffer and thus is less able to withstand the build-up of pressures. When the delay period is within the first 24 hours then a longer duration results in less damage.

The cement type and sulphate content of the cement is important. For the same treatment, the high-early-strength cement is damaged, while the sulphate resistant cement is not (even at 100°C maximum temperature and when 4% additional sulphate is added to the sulphate-resistant cement).

Use of 8% ground limestone to HES cement neither diminishes nor increases the extent of the problem. On the other hand, trass, ash and slag when used to partially replace some cement (30% to 50%) substantially improved performance; no damage was observed after 10 years storage. Five to ten percent mass replacement by fume also resulted in a clear reduction in expansion.

Heinz and Ludwig postulate that the composition of cement is very important in determining whether expansions will occur. In particular, the main influence derives from the SO₃/Al₂O₃ ratio of the cement. However, the sulphate proportion appears to have a higher weight in determining behaviour; therefore, the authors suggest that the ratio (SO₃)²/Al₂O₃ is a parameter that shows the strongest correlation to subsequent effects of secondary ettringite formation. In this ratio the alumina content is that contained in C₃A only — i.e. the so-called “active” alumina.

Figure 5.11 is a scattergram of expansion vs $S²/A$ ratio. All data for various cements are plotted. The authors suggest a “Safe Ratio” of 2.0 — cements with a smaller ratio than 2.0 are not susceptible to secondary ettringite attack. Note that at higher $S²/A$ ratios expansion is again lower. In other words, there appears to be a pessimum ratio where expansion and damage are a maximum.

One other important finding from these authors is that inclusion of 14% air-entrainment into the mortar “drastically” reduces expansion; ettringite formation occurs, but takes place in the air-void system rather than within the confined space of the pore structure. On the other hand, if a potential exists for secondary ettringite formation, a material that undergoes freeze/thaw cycles is likely to be damaged to a greater extent. After such damage Heinz and Ludwig observed AFT crystals on aggregate particles. Cracks also occur in the matrix; in these cracks ettringite crystallizes at right angles to the crack edges.

5.6 1990 — Lawrence et al [177]

The test programme at the British Cement Association was performed primarily in an attempt to confirm German observations of secondary ettringite formation; U.K. cements were used.

Prisms, 40x40x160mm, were cast in accordance with RILEM standard. The mortar composition was 1:3:0.5 cement/sand/water. Twenty U.K. cements, mostly commercial rapid-hardening cements were employed. A pre-curing period of 2 hours in the moist room was used. Specimens were then placed in a water bath and the temperature was raised to 100°C over the course of two hours. The boiling environment was maintained for another 3 hours and specimens were then al-
EXPANSION, mm/m

Suggested "Safe Ratio" of 2.0. Cements with ratio less than 2.0 not susceptible to secondary ettringite attack.

S-303 CONTENT
A = Al2O3 CONTENT
IN C3A ONLY (ACTIVE)

Figure 5.11
Scattergram of S/A ratio vs. Expansion (data from ref. 133)

Allowed to cool naturally until 16 hours when they were stored in water at 20°C. The severe treatment was chosen to reveal damage in the shortest amount of time; the regime chosen is more "extreme" than is likely in practice.

Examples of expansive and non-expansive results are shown in Figure 5.12; other results are given in Figure 5.13. Lawrence et al. were able to classify the types of expansive behaviour into 7 categories:

(a) zero expansion — e.g. cement ES3579, Figure 5.12
(b) small continuous expansion
(c) small accelerating expansion
(d) large accelerating expansion — e.g. cement ES3594, Figure 5.13
(e) decelerating or limiting expansion
(f) large S-shaped expansion leading to a definite maximum — e.g. cements ES3595 (Fig. 5.12) and ES3572 (Fig. 5.13).
Figure 5.12
Typical Expansion vs. Time Curves (data from ref. 177)

Figure 5.13
Expansion vs Time Curves Showing Effect of Delay Period (data from ref. 177)
Table 5.2
Expansion vs. Sulphate Content (ref. 177)

<table>
<thead>
<tr>
<th>TOTAL SULPHATE %</th>
<th>ADDED SODIUM SULPHATE %</th>
<th>MAXIMUM EXPANSION %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.00</td>
<td>0.00</td>
<td>0.03</td>
</tr>
<tr>
<td>4.00</td>
<td>1.00</td>
<td>0.70</td>
</tr>
<tr>
<td>4.64</td>
<td>1.64</td>
<td>1.10</td>
</tr>
<tr>
<td>5.27</td>
<td>2.27</td>
<td>1.50</td>
</tr>
</tbody>
</table>

The addition of 1% $SO_3$ to cement ES3578 changed its behaviour from a class (e) to a class (b) category — the addition of sulphate removed the tendency to reach a limiting expansion and resulted in a more gradual expansion process.

The addition of sodium sulphate to some cements did not change the time at which expansion started, but the magnitude of the maximum expansion increased as sodium sulphate content increased. Table 5.2 shows this effect.

Figure 5.13 illustrates the influence of duration of heat treatment on subsequent expansion. Specimens that were heat-treated for 16 hours, rather than 3 hours showed a reduction in the time to the start of expansion. The effect is pronounced for cement ES3740; the cement that showed very little expansion when treated for 3 hours showed the maximum expansion when treated for 16 hours.

Petrography indicated that for specimens which cracked, the cracks were filled with ettringite. Ettringite also formed ridges around surface cracks. Expansion did not necessarily mean that the specimens cracked, however; some bars showed as much as 1.2% expansion without cracking.

Analysis of thin sections showed rims of ettringite around sand grains. An “acicular” ettringite morphology existed within these rims.

Lawrence puts forward a number of points to explain secondary ettringite formation:

- Any ettringite that forms during the delay period decomposes during heating at 75°C or above
- Water storage at room temperature after heat treatment results in the re-formation of ettringite without significant changes in the quantity of monosulphate. For ettringite to form in preference to monosulphate the pore solution must be high in sulphate content. Lawrence proposes that this is the result of modification of the calcium aluminate hydrates — hydrogarnet like materials — during heat treatment; the modified aluminate compounds cannot rapidly absorb sulphates and allow free sulphate ions, such as those slowly released by C-S-H to persist in solution.
- The natural process of slow release of aluminates with time then results in ettringite crystallization from solution.
- A less severe temperature regime does not modify all of the aluminates. Some can rapidly absorb SO$_4$ immediately on cooling. Monosulphate then forms instead of ettringite because there is insufficient sulphate in solution.
- Ettringite formation occurs at nucleation sites: on the surface of voids, in microcracks and at the cement-aggregate interface.
- The air-voids or flaws must become filled in order for internal stress and concrete disruption to occur.
The first important works directly related to secondary ettringite formation were performed by Ghorab et al in 1980. They found delayed expansions when specimens were cured at temperatures greater than 80°C. Heat treatment was found to be an essential component if expansion during soaking was to occur, but the time at which the treatment occurred was found not to be very important. In many respects the work done at the Cement Industry Research Institute [268] supported these initial findings.

The work of Heinz & Ludwig, reported in 1987 and later in 1989 firmly established the phenomenon of secondary ettringite formation. They found several crucial factors influencing the potential formation of secondary ettringite:

- the critical heat-treatment temperature above which damage could potentially occur is in the range 70-75°C
- the longer the delay period within the first 24 hours, the lower is subsequent expansion. However, delay periods of several days or weeks, followed by heat treatment, could also produce sufficient cracking to provide the nucleation sites necessary for secondary ettringite effects
- the cement type and particularly the ratio of sulphates to aluminates are important for determining the potential for secondary ettringite formation. In 1987 Heinz & Ludwig established that an $S/A$ ratio of 0.67 appeared to be a “critical” ratio above which substantial expansion and cracking had the potential to occur. In 1989 Heinz et al established another ratio, $\sqrt{S}/A$ (where $A$ is the “active” alumina contained in $C_3A$); the safe value for this ratio was determined to be 2.0.
- the time at which significant expansion starts and the rate of expansion is a function of specimen size. Although the research was fairly limited in this respect, it appears that the larger the specimen (or member), the longer is the time to start of expansion, and the slower is the rate of expansion. If Heinz and Ludwig’s interpretation is correct, it explains why expansions and cracking in the field have been observed after several years, while laboratory experiments, on smaller samples, show large expansions after the first two or three years of soaking.
- air-entrainment of the mortar phase drastically reduces the expansions that are observed when comparison is made to a non-entrained mortar. This phenomenon has been observed by several researchers and indicates that one simple method of deterring damage due to potential secondary ettringite formation may be to ensure that adequately entrained concrete is cast.
6.1 Effect of Gypsum Content of Cement on Strength and Volume Stability

Retardation of set and early strength requirements are both important practical considerations that call for the production of cement with an “optimum” gypsum content. The fineness of the cement plays an important role in this respect and affects both retardation and early strength gain; the amount of gypsum required to produce proper retardation is higher the higher the fineness [180]. In 1917 ASTM C19-17 limited SO$_3$ content to 2%; considering that current Type 30 (and occasionally Type 10) cements are ground above 600 m$^2$/kg Blaine, the 2% SO$_3$ limit is clearly not acceptable. Current CSA standards allow 4.5% SO$_3$ or more.

A perusal of the Chapter 5, and some further test results given below, indicate that what is “optimum” for strength and retardation is not necessarily (and perhaps not normally) optimum with respect to long-term stability of concrete.

6.1.1 Test Results of Al-Rawi [6]

The most significant work in this area was performed by Al-Rawi in 1977 [6]. The rate of formation of sulphoaluminate is accelerated by an increase in temperature. Therefore, one might expect that the optimum SO$_3$ content for maximum strength to increase as temperature increases. Brown [34], for example, noted that maximum strength was achieved in a heat-cured concrete with 7.1% SO$_3$. However, such concretes exhibited high expansions and he noted that it may be necessary to limit SO$_3$ to 5–6% to keep expansions to a tolerable level.

Al-Rawi examined the strength and expansion of concretes made with two different clinkers. Both clinkers (Table 6.1) had high C$_3$A and C$_3$S contents which are believed to be beneficial to steam-curing.

The clinkers were blended with gypsum to give SO$_3$ contents of 2.0, 3.8, 5.7 and 7.5%. Concrete cubes and prisms were cast with w/c=0.5, and a/c=5. Specimens were subjected to an 18 hour curing cycle consisting of 4 hours delay, a 12°C/hour heating rate to either 50, 70 or 90°C, followed by 6 hours of curing. Strengths were determined immediately after cooling. Other specimens were fog cured for ages up to 182 days. Deformation readings on prisms were taken to an age of 48 weeks.

Strengths at ages of 28 and 182 days are shown in Figures 6.1 and 6.2 (the notation C1-70A means concrete made with cement 1 heat-cured at 70°C). Both figures indicate that the cements should have between 3.8 and 5.7% SO$_3$ content to produce optimum strengths of heat-cured.

<table>
<thead>
<tr>
<th>Compound Composition of Clinkers used in Al-Rawi Study [6]</th>
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<tbody>
<tr>
<td>Cement#</td>
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<tr>
<td>C1</td>
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<td>C2</td>
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Figure 6.1
Dependence of 28-day Strengths on SO₃ Content and Curing Temp. (data from ref. 6)

Figure 6.2
Dependence of 182-day Strengths on SO₃ Content and Curing Temp. (data from ref. 6)
specimens. On the other hand room-cured concretes show a clear regression in strength as SO₃ content increases above 2%. General conclusions, however, should not be made upon the basis of only two high C₃S content cements.

Optimum SO₃ contents for strength are not necessarily compatible with optimum contents for volume stability. Figure 6.3 shows that SO₃ contents above about 4% result in large expansions within the first 20 weeks of water-curing. On the other hand, results shown in Figure 6.4 indicate that an 18 hour heat-treatment can reduce expansion during 48 weeks of water-soaking.

The results given in Figure 6.4 are contrary to the commonly-held view that heat-treatment produces an increase in expansion due to secondary ettringite formation. Damage due to SEF has been connected to the production of microcracks during heat-treatment. Such cracks are reduced, or eliminated, by providing an adequate pre-curing period. Note that Al-Rawi employed a 4 hour pre-cure prior to heat-curing to as high as 90°C.

### 6.2 The Practical Significance of the SO₃/Al₂O₃ Ratio

For Type 30, high early strength cement, CSA A5-M88 allows a maximum of 3.5% SO₃ when the C₃A content is less than or equal to 7.5%, and a maximum of 4.5% if C₃A content is greater than 7.5%. The American Society for Testing and Materials Standard C150-89 also allows as much as 4.5% SO₃, but the C₃A limit above which this is allowed is 8%, rather than the 7.5% found in the CSA standard. Many other Countries in the world follow the American standard, while others set a single SO₃ limit varying from 3.0 to 4.5%. [Cembureau, Cement Standards of the World, 46].

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**Figure 6.3**

Effect of SO₃ Content on Expansion of Normal Fog-Cured Specimens (data from ref. 6)
Canada, Colombia and Hungary are the only three countries noted in the Cembureau report that allow 4.5% SO$_3$ in cements which contain as little as 7.5% C$_3$A (Colombia and Hungary set a 4.5% SO$_3$ maximum which is independent of C$_3$A content). Canada and those countries that use ASTM C150-89 also permit SO$_3$ contents greater than 4.5% if it can be shown that mortar bars prepared in a standard manner and soaked in water for 14 days expand less than 0.02%. Thus, a low expansion value in a 14 day test is used to assess the long-term volume stability of cements with high sulphate contents. The question that arises is: is a 14-day test an adequate method to predict long-term stability?

Lerch and Ford in 1948 [183] tested prisms made from 27 different cements that were moist-cured for 1 day and then stored continuously in water at 21°C for 5 years. The SO$_3$ contents of the cements were fairly low, but the results, shown in Figure 6.5 point out the lack of correlation between expansions at 14 days and expansions at 5 years. Several cements show less than 0.02% expansion at 14 days, but show appreciable expansions at 5 years. The test results help to accentuate that prediction of long-term behaviour from short-term tests is seldom reliable. In the case of Lerch’s results, the reliability is low.

Although the S/A ratio appears to be the most reliable “indicator” of whether secondary ettringite formation could be important, note that other factors also contribute to the determination of whether a given cement is likely to be stable in concrete. Wells et al, for example proposed that it is not just the S/A ratio that determines whether expansion occurs after heat treatment; both a low ratio and a low alkali content are necessary to avoid large expansions [317].

Chen and Grattan-Bellew [55] in their study of alkali-aggregate reaction added various quantities of K$_2$SO$_4$ and Na$_2$SO$_4$ to a clinker from a single cement plant. A suite of 17 cements was manu-
factured which contained various alkali contents. The cements were interground with an optimum quantity of gypsum to a fineness of 370 m²/kg. Expansion was then monitored with time of storage in a moist environment. A good correlation (r=0.91) was found between acid-soluble alkali content and expansion. However, further analysis of the data for the present report also showed a positive correlation between expansion and MgO content (Figure 6.6) and between rate of expansion and SO₃/Al₂O₃ ratio (Figure 6.7); both correlation coefficients (0.73 and 0.80) are significant at the 5% level.

Chen & Grattan-Bellew also considered the potential effect of sulphates and looked at the hypothesis that “ettringite in cracks and air-voids might be contributing to the late stages of expansion”. They found that there was no correlation between rate of expansion of the high-expansion bars (those with Na₂O equivalent >1.0%) and the amount of ettringite in the mortar at 6 months.

6.3 Specifications for Heat Treatment of Concrete

Concern over possible problems with secondary ettringite formation has prompted some researchers to recommend heat-treatment guidelines, some authorities to change their specifications, and some authorities to consider changing their specifications. Proper heat-treatment methods would theoretically eliminate, or substantially reduce, the potential for problems even if the cement and/or aggregate were found to be inferior.

Neck [237] proposed three types of heat treatment, depending upon the proposed durability exposures, with the objective of avoiding damage due to secondary ettringite formation:

- Type I: 1 hour pre-cure with a maximum soaking temperature of 80°C — for interior exposures with no moisture
- Type II: 2 hour pre-cure with a maximum soaking temperature of 70°C — for exterior exposure with no contact with the earth
CORRELATION BETWEEN EXPANSION AND MgO CONTENT
17 POINTS, CORR. COEFF. = 0.732
EXPANSION = 0.651 + 5.974 * MgO

Figure 6.6
Scattergram of Expansion vs MgO Content (data from ref. 55)

SO3/Al2O3 RATIO VS. EXPANSION
17 cases; r=.798
EXPANSION = -15.513 + 47.297 * S/A RATIO

Figure 6.7
Scattergram of SO3/Al2O3 Ratio vs Expansion (data from ref. 55)
- Type III: 3 hour pre-cure with a maximum soaking temperature of 60°C — for exterior exposure with contact with the earth

The European Committee for Standardization, in 1989 has responded to the issue by setting more stringent specifications for the heat treatment of concrete [98]. These are:

- The concrete temperature during the first 3 hours of curing cannot exceed 30°C and cannot exceed 40°C during the first 4 hours
- The rate of temperature rise cannot be greater than 20 °C/hr
- The average maximum temperature cannot exceed 60°C; individual temperature readings cannot exceed 65°C
- The cooling rate after heat-treatment cannot exceed 10 °C/hr
- Concrete must be protected against moisture loss

Also in 1989, The German Committee for Reinforced Concrete [103] recognized that intensive heat treatment can affect durability of structural members exposed to weathering. Faults in the concrete due to too rapid warming or sharply differing expansion are susceptible to "sulphate bonding [that] can occur with a high level of moisture in the concrete". Accordingly, specifications for damp conditions are different for dry concrete, as shown in Table 6.2. The 60°C maximum temperature for concrete that will be damp in service is clearly a change made to address potential problems with secondary ettringite formation.

The British have been slower to respond, perhaps because they have been waiting for detailed research results from the British Cement Association (e.g. Lawrence et al [177]). It is interesting that the British code of practice in 1972 CP110:1972 noted that damage due to excessive heat treatment would not occur if:

- temperature rise during the first 3 hours is not greater than 15°C/hr
- thereafter, the rate of increase or decrease is not greater than 35°C/hr
- the maximum temperature reached by the concrete is not greater than 80°C.

However, the 1985 British code of practice BS8110:1985 omitted the above three guidelines. Other British authorities have taken steps to fill the gap. The British Dept. of Transport Specifications for Highway Works (1986), Part 5, Clause 1709:5(ii) requires (1) the concrete must be left for 4 hours without additional heating; (2) the concrete temperature cannot be raised at a rate

| Table 6.2 |
| Specification for Heat-Treated Concrete |
| German Committee for Reinforced Concrete, 1989 [103] |

<table>
<thead>
<tr>
<th>Moisture Category</th>
<th>Dry</th>
<th>Damp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum holding (delay) period (hrs)</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>+ or +</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Maximum concrete temperature during holding, °C</td>
<td>≤20*</td>
<td>≤20*</td>
</tr>
<tr>
<td>Maximum concrete temperature**, °C</td>
<td>80</td>
<td>60</td>
</tr>
</tbody>
</table>

* heating rate should be reduced to 10 °C/hr for lightweight concrete

** individual values may be up to 5°C higher
greater than 20°C/hr; (3) the maximum concrete temperature cannot exceed 70°C; (4) the rate of cooling cannot exceed the rate of heating [177].

In North America measures to control excessive heat treatments have been taken on a local scale. The results of Merritt & Johnson [218] on concrete strength development after various heat treatments were incorporated into the Iowa State Highway Commission specifications for precast concrete:

- The initial concrete temperature should not be greater than 38°C for a minimum of 2 hours after casting
- The rate of temperature increase after a 2 hour period should not be greater than 14°C
- The maximum temperature attained should not be greater than 66°C
- The maximum temperature should be held for a period sufficient to develop the required strength
- The rate of temperature decrease should not be less than 11°C/hr.

Units should be kept covered for at least 24 hours after casting.

This is all good, practical, engineering sense; it was not intended to address directly the issue of prevention of secondary ettringite formation. There is some concern, however, that such steps should be taken immediately, and by national authorities.

Hill [136], points out in a letter to ACI committee 517.2R, the issues that need to be addressed concerning guidelines for precast concrete manufacture. He notes that the present guidelines do not mention the current potential problems related to secondary ettringite formation of precast concrete. The three conditions that appear necessary for this problem to surface need to be included in a warning statement. These conditions are:

- a curing (heat-treatment) temperature greater than 60-71°C
- concrete that will be submerged or exposed to 100% relative humidity
- concrete made with a cement with a high S/A ratio and high alkali contents.

Hill was concerned that under the guidelines noted in 517.2R a user could face a situation where the above three conditions occur. Hill recommended that the current document be withdrawn.

It appears that in Canada a revision of CAN3-A23.4-M78 on precast concrete methods is about to take place. The 1978 standard specifies that the concrete should attain initial set before heat is applied (this is normally 2 to 4 hours but could be as low as 45 minutes). During this time the concrete must be maintained at at least 10°C. Temperature increase should occur at approximately 20°C/hr to an optimum temperature range of approximately 65-70°C, but in no case should the curing temperature exceed 80°C. Temperature decrease should not occur at a rate exceeding 30°C/hr. Proposed changes for the new version of A23.4 include reducing the maximum temperature from 80°C to 70°C.

6.4 Comment

Determination of “optimum” gypsum content involves the determination of the proportion of gypsum that will produce optimum strength and a satisfactory setting time. Research performed in Europe and in Canada (see Chapter 7) indicates that the sulphate/alumina ratio of the cement may play an important role in determining long-term stability of concrete. Thus, “optimum” gypsum
needs to be redefined; long-term durability of products manufactured with Portland cement needs further consideration.

Clearly, cement is just one ingredient of concrete. Other ingredients can affect durability as can the mix-design, casting and curing procedures. However, all other factors being satisfactory, it is necessary to be able to evaluate cements for long-term durability. This requires that a satisfactory test method is available.

It is unrealistic to expect a good correlation between the expansion of mortar bars soaked in water for 14 days and expansion and/or cracking of concrete at 10 or 15 years. The scattergram of Figure 6.5 showed one example of the poor correlation that exists between short and long-term expansions; the cements were manufactured at mid-century. It is highly unlikely, for a number of reasons, that the correlation for modern cements is better.

The viability of the 14-day soaking test should be re-examined in the light of the chemistry and physical properties of modern cements. This is especially important given (a) secondary ettringite formation may be an important durability issue, and (b) both ASTM and CSA standards allow more than 4.5% SO₃ if a cement can be shown to pass the 14-day sulphate expansion test.

In Canada, A23.4 specifications for precast concrete are presently under revision. It is suggested that careful consideration should be paid to the potential secondary ettringite issue and to the German specifications (Table 6.2) that have addressed this potential problem. It is especially troublesome that the proposed A23.4 still relies on the setting time to define the minimum delay period prior to treatment; this setting time could be as short as 45 minutes and still satisfy both A23.4 and A5 standards.
Chapter 7

Rapid Test Method for Secondary Ettringite Formation

Researchers have been looking for rapid test methods to "predict" long-term behaviour of concrete for many years. For example, in 1949 Scholer [282] reported on results of a revised accelerated performance test which was first developed by Gibson in 1932; Gibson wished to look at the map-cracking of concrete pavements [108].

In Scholer's test method, saturated concrete specimens (3"x4"x16") are dried at 54°C for 8 hours, then immersed in water at 21-27°C for 16 hours. This process is repeated for 6 days a week while on the seventh day they rested — immersed in water. This accelerated test can be performed for as long as the researcher wishes, with expansions being measured at regular intervals.

To substantiate his test method, Scholer compared field performance of various concretes to accelerated performance. Concretes were made with 2 types of aggregate (one good performance, one poor performance) and a wide variety of cements. Prisms (3"x4"x16" prisms — the same size as those used in the accelerated test) were placed on the ground and exposed to 5 years of natural freeze/thaw cycles. The accelerated exposure was run over 285 days. Figure 7.1 shows that a positive correlation between field and accelerated performance occurred. Failure of the specimens occurs by excessive expansion, cracking and loss of strength.

It is interesting to note that as early as 1949 there is some inference that something other than the known reaction/expansion processes (such as aar) may be at work. For example, Scholer recognized the importance of the bond between the paste and the aggregate and that after this bond fails, a "jacking action" tends to develop to increase expansion.

Although Scholer achieved good correlations between laboratory and field performance, and his work was heralded as landmark research (by Bryant Mather, for example [see discussion to paper]), the "accelerated" exposure lasting 285 days would hardly be considered "accelerated" today. In recent times, many other researchers, including the present author, have attempted to develop laboratory tests that reflect long-term field performance. The primary difficulty in this development is that it takes a very long time to determine whether an accelerated test is accurate because it takes a very long time to obtain relevant field data.

An adequate test must ensure that it "measures" or predicts potential expansion in an unbiased fashion. Figure 5.13 (Chapter 5) illustrates the influence of duration of heat treatment on subsequent expansion. Specimens that were heat-treated for 16 hours, rather than 3 hours showed a reduction in the time to the start of expansion. The effect is especially pronounced for cement ES3740; the cement that showed very little expansion when treated for 3 hours showed the maximum expansion when treated for 16 hours. The development of a rapid test method must take this into account [177].

Observations by Heinz et al that freeze/thaw cycling exacerbates any potential for secondary ettringite formation and damage, leads them to the suggestion that freeze/thaw cycling can be used to accelerate potential deterioration of concrete that has a dense microstructure [133]. However, they did not attempt to develop an accelerated test method based on this principle.

7.1 The Duggan Test

One accelerated test method that has been extensively developed will be the subject of the remainder of this chapter, because it is purported to "measure" the effect of secondary ettringite formation of various concretes. This is the Duggan test, whose development, results, and
0.25
0.2
0.15
0.1
0.06
0

DATA FROM SCHOLER, 1949
45 cases; CORR. COEFF. = .767
FIELD EXP. = -.017 + 1.382 * ACCEL. EXP.

Figure 7.1
Scattergram of Accelerated vs. Field Expansions (data from ref. 282)

significance of results have been reported in detail in Duggan & Scott [91-93]; Scott & Duggan [284]; Gillott et al [110, 111]; Jones & Gillott [155]; Attiogbe et al [12]; and Wells et al [317].

As originally devised the Duggan test involves the following procedure [284]:

- Concrete cores (5 minimum) are taken from a structure or from laboratory-cast prisms or cylinders. The cores are 25mm in diameter and at least 65 mm long and are cut to 50mm lengths. The ends are ground smooth and parallel.

- Initial length measurements are taken with a comparator just before the start of heat treatment. In later tests by Duggan & Scott and in tests by Gillott et al [110,111] this measurement was used as the zero point from which other strain readings were taken.

- Cores are soaked for 3 days in distilled water @21°C in a closed container

- Cores are then placed in a dry-air oven at 82°C for one day

- Cores are removed from the oven, allowed to cool for 1 hour, then placed back in distilled water for one day
A second one-day heating, one-day soaking cycle is performed
A third cycle is performed, but this time cores are left in the oven at 82°C for 3 days
At the end of the third heating cycle, cores are removed from the oven, allowed to cool for 1 hour and then length measurements are taken relative to a steel standard. In the early tests by Duggan and Scott this measurement was used as the zero point for further strain readings.
Cores are placed in distilled water at 21°C
Length measurements are taken relative to the steel standard at intervals of 3-5 days.

7.1.1 Significance of Duggan-Test results

The test was initially thought to be an accelerated means by which potential alkali-aggregate reactivity of various cement/aggregate combinations could be assessed. Scott & Duggan set about establishing that the Duggan test successfully predicted aar of various lab-cast concretes. By taking cores from both sound and deteriorated site concretes, they also established a rough correlation between observed behaviour and results of the Duggan test. Presumably due to time/financial limitations, no attempt was made to establish a formal correlation between Duggan results on young concretes and the long-term performance of those concretes. Scott & Duggan [284] noted that the test could be used both to classify lab trial mixes, and to evaluate existing structures.

Observations that (a) concrete known to be susceptible to aar and concrete especially prepared with reactive aggregate showed large expansions in the Duggan test and (b) concrete with small expansions in the Duggan test did not contain alkali-reactive aggregate, led the researchers to conclude that the test could be useful for evaluating potential alkali-aggregate reactivity.

Later research (Duggan & Scott, 93) showed that both the type of aggregate, the type of cement and the alkali content of the cement play a role in determining the 20-day expansion value (which was defined by the researchers as the critical time at which pass/fail criteria could be established). Figure 7.2 shows some of the results. Duggan & Scott concluded that only concrete should be ranked by the Duggan test — it is the cement/aggregate combination, and not just the cement alkali content or the extent of reactivity of the aggregate that determines potential expansion behaviour. They advocated performance testing, exemplified by the Duggan test, such that “the testing emphasis currently placed upon acceptance or rejection of aggregates should be shifted to acceptance or rejection of concrete”. In this regard, the researchers should be commended for espousing a philosophy that is starting to gain wide acceptance; a significant number of researchers, the present author included, believe that it is a dangerous and potentially costly practice to accept or reject the individual material components of concrete, such as aggregate, cement and pozzolan in isolation.

7.1.2 Research of Gillott, et al

The research of Gillott et al [110, 111] and Jones et al [155] provides valuable insight into the significance of the Duggan test.

In the first series of test, [111], various concretes were manufactured with 4 commercial cements with different alkali contents, 2 alkali active aggregates and 1 inert aggregate. Specimens were subjected to both the Duggan test and to the standard concrete prism test for Potential Expansivity of Cement/Aggregate Combinations (CSA A23.2-14A).
Through careful experimentation and comparisons of the response of the various concretes to the two types of test, Gillott was able to make the two primary conclusions that:

- alkali-aggregate reaction is not the major cause of expansion measured during the first 21 days of the Duggan test
- expansion in the Duggan-test at ages up to 90 days "correlates with the relative proportion of ettringite and frequency of microcracking in the concrete".

Other more tentative conclusions were that (a) Duggan-test expansion depends primarily on the properties of the cement, and (b) the form of the sulphate that is present (either gypsum or anhydrite) may affect the extent of microcracking caused by the Duggan test, and thus may affect subsequent expansions.

In a second set of experiments, reported in detail in Gillott et al [110] both cement pastes and concretes were manufactured from various cements and aggregates. Six different Type 30 Portland cements were chosen on the basis of variations in SO₃ content. Two non alkali-expansive aggregates were used in the preparation of the concrete. Cement pastes were prepared for each of the six cements, with a w/c ratio of 0.4. Ten concrete mixes were prepared with different cement/aggregate combinations; the nominal cement content was 475 kg/m³, and the water/cement ratio was approximately 0.4 for all concretes. All specimen sizes were 3"x3"x14" and, in an attempt to simulate precast concrete, specimens were subjected to an accelerated curing regime of: 2 hours pre-cure, 2 hours temperature increase to 85°C, 4 hours at 85°C, and slow cooling overnight. The 24 hour strengths of the concretes were in the range 27-44 MPa, while the 28 day strengths were in the range 56-64 MPa.
Figure 7.3
Expansion of Hardened Cement Pastes and Concretes Made with the Same Cements
(data extracted from ref. 110)
Gillott found that all cement pastes had significant expansion after being subjected to the Duggan régime. All pastes (Figure 7.3) showed a monotonically decreasing expansion over the course of 90 days of soaking. The initial and final expansion values and the rate of expansion over various time periods was different for the different cements.

All ten concretes that were tested also showed significant expansions during the Duggan test. It is understandable that after Gillott’s findings were released, those in the cement and concrete industry became rather concerned about the Duggan test; Five of the six concretes made with the Nelson aggregate (a dolomitic limestone) failed the proposed Duggan limit of 0.05% at 21 days, while two of the four concretes made with Exshaw aggregate (a calcitic limestone) failed.

The results presented by Gillott provided an opportunity to compare the expansion behaviour of pastes and concretes. Figure 7.3 shows the expansion of cement pastes and of concretes manufactured with the same cements at approximately the same water/cement ratio. The aggregate used to make the concretes was the Nelson dolomitic limestone.

There is a fair correlation between the expansion of pastes and the expansion of “equivalent concretes” at soaking times up to approximately 40 days. Beyond 40 days, however, behaviour between the two “types” of material is different. The expansion curves for pastes become concave downwards — the expansion process is starting to exhaust — while the curves for concrete remain straight or, in the case of the concrete with Cement D, become concave upwards. The concrete strains at 90 days for two of the concretes are much greater than those of the corresponding cement pastes. The lack of correlation at higher expansion levels is clearly shown in the scatter-
gram given in Figure 7.4; this is a plot of expansion of concrete vs. expansion of the equivalent cement paste at a given time.

Based upon an examination of the research noted in this report, it is suggested that the reasons for the disparity between paste expansion and concrete expansion are that with time ettringite becomes more concentrated in localized regions such as in microcracks and at cracks at the aggregate/paste interface. The total ettringite content in the concrete matrix is the same as in the paste, but in the concrete ettringite is localized and is therefore more efficient in producing expansions.

By using a suite of cements with various sulphate and aluminate contents Gillott was, in essence, able to confirm the findings of Heinz et al [133] (see Figure 5.11, Chapter 5) who noted a pessimum value for $S^2/A$ ratio and that cements with high $S^2/A$ ratios showed smaller expansions than those with smaller ratios. Figure 7.5 plots expansions vs $S/A$ ratios for both cement pastes and concretes (made with Nelson aggregate). There appears to be a pessimum range for $S/A$ molar ratio centred about a value of 1.0.

One important aspect of the test programme was that the expansion tests that were performed on concrete in the Univesity of Calgary laboratories were repeated in the CN laboratories. It is significant that when one compares both the qualitative behaviour of expansion vs. time and the sizes of expansions observed at given time, there is excellent agreement between the results from the two laboratories; the Duggan test on concrete appears to have excellent reproducibility.

Gillott’s research resulted in a number of practical conclusions:

- Delayed ettringite formation is the major cause of expansion of cements and concretes exposed to the Duggan test
- The cement is the main component causing expansion; expansion is highest, all other factors equal, when the $S/A$ molar ratio is approximately 1.0 (Note that the present author has attempted to correlate oxide compositions and Blaine surface areas of cements used in Gillott’s work and in Attiogbe’s work with expansion. Various correlation methods have met with failure; there does not appear to be single parameter or group of parameters which show significant correlation — other than the $S/A$ ratio).
- The severe heat treatment of the Duggan test causes microcracks in the concrete. Ettringite can form faster due to easier penetration of water and an increase in the number of potential nucleation sites.
- The formation of ettringite at nucleation sites effects further microcracking and affects expansion rates.

### 7.1.3 Research of Attiogbe and Wells et al [12, 317]

Attiogbe also examined the use of a severe heat treatment followed by soaking in water and measurement of expansion to evaluate the cements and concretes with potential durability problems. The researchers prepared 75x75x380mm prisms of concrete and 150mm cubes of both concrete and cement paste. The water/cement ratio for the pastes was 0.50. Specimens were stored at 23°C in a moist room for the first 24 hours after casting, then in a fog room until 7 days.

Unlike Gillott’s test programme, a simulated precast heat-treatment regime was not used prior to the start of test. The “Duggan test” performed by Attiogbe normally consisted of two cycles of (a) heating to 80°C for 3 days, followed by (b) 1 hour cooling to room temperature, and then (c) soaking in distilled water for 2 days. The Duggan test and the Attiogbe test are compared in Figure 7.6. Note that Attiogbe defined “zero strain” two days after the end of the last heating period (see Figure 7.6). In other respects the Attiogbe test method was similar to the Duggan test.
Figure 7.5
Observations of a Pessimum SO₃/Al₂O₃ Ratio at Various Ages (data from ref. 110)
Figure 7.6
Temperature Testing Régimes, Data and Examples Strains in Duggan and Attiogbe Tests
Example expansion results for cement pastes are shown in Figure 7.7. Note the extremely large expansions that were observed with the pastes made with cement B and cement C.

The parallel tests performed by Attiogbe are perhaps more interesting than the main series. The researchers looked at expansion behaviour of pastes and concretes stored in saturated NaCl solution rather than in water. Companion specimens stored in water expanded, but specimens stored in NaCl did not expand and even contracted in some cases. In the presence of chlorides the solubility of ettringite increases; therefore, no ettringite is observed in NaCl soaked specimens and no expansion occurs. This is strong evidence that the expansions in water are due to the formation of ettringite.

Fundamental examinations confirm that pastes and concretes that exhibit large expansions contain “massive formations of ettringite” and those with small expansions have “little or no visible amounts of ettringite”. The results suggest that “late formation of ettringite” is the cause of expansion. Attiogbe’s research is in agreement with Gillott’s in this respect; the Duggan test, or tests similar to Duggan’s test, indicates expansion due to ettringite formation and not alkali-aggregate reaction.

### 7.1.4 Correlations Between Gillott’s and Attiogbe’s Results

Both research programmes have come to similar conclusions concerning the Duggan test. The test is a measure of secondary ettringite formation and not alkali aggregate reaction, at least in the first 20 days of soaking. Furthermore, the findings in both studies do not contradict the
mechanism of secondary ettringite formation first proposed by European researchers (see Chapter 5).

Attiogbe and Gillott used some of the same types of cement in their studies. Thus, it is possible to examine whether any correlation exists in the expansions obtained by the two studies. Figure 7.8 shows a scattergram that was obtained from the available results.

The very large strains shown in the Attiogbe study and confirmed by Wells et al [317] are somewhat surprising. Apparently the Attiogbe heat-treatment régime is much more severe than that of the Duggan régime. This is also somewhat surprising, since Gillott subjected his specimens to a simulated precast régime prior to the Duggan test. One aspect that could explain the very high strains of the Attiogbe paste specimens is the higher w/c ratio used (0.5 vs 0.4 for Gillott).

In any event, there is little correlation between these two studies, despite the fact that the same types of cement were used. Although it has been shown that the Duggan test is reproducible among laboratories, it is clearly important that a single test procedure is used for all studies.

### 7.2 Interpretation of Duggan-Test Results

Duggan & Scott initially proposed a limit of acceptable behaviour for concrete as 0.1% expansion after 20 days of soaking. The proposal of this limit for the Duggan test was criticized. Lawrence et al [177], for example, had several concerns about the test which they say prevent satisfactory interpretation of results:
22mm diameter cores are not representative of the concrete structure. The testing of small concrete cores could magnify the intensity of the effect of secondary ettringite formation. Note that Lawrence tested mortar bars which are also not representative of the concrete.

Drilling cores could itself produce damage and thus create sites for additional expansion of ettringite.

Site concretes may not have been heat-treated and therefore may not be susceptible to secondary ettringite formation. They become susceptible when the core is heat-treated in the Duggan test.

Expansions of the cores during testing may be the result of a number of different effects.

The heating cycle proposed by Duggan does not represent practical heating regimes. The heating programme is very severe and may result in the rejection of cements that may perform adequately in practice.

Duggan’s test results have not been correlated with field concrete.

7.2.1 The Zero Strain Datum

A primary criticism centres about the definition of zero strain on a dry datum. Figure 7.6b shows a schematic of the heating/cooling regime followed in the Duggan test. Also shown (Figure 7.6c) are example values of observed strains measured at the end of each component of the Duggan test and during soaking (typical values extracted from Duggan & Scott [92]). Figure 7.6a shows the temperature regime followed by Attiogbe et al [12].

In this example, first drying results in a shrinkage strain of about 0.07% (bottom left of Figure 7.6c). Most, but not all, of this deformation is recoverable on first resaturation. Second drying produces less relative shrinkage than in the 1st cycle, but the total shrinkage is slightly greater. Second resaturation is not much different than 1st resaturation and the magnitude of 3rd drying is approximately the same as second drying.

The length of the specimen at the third drying point is the definition of zero strain first used by Duggan. Thus, when bars are placed back in water for swelling vs. time measurements, a substantial component of that swelling deformation is due to the uptake of water and not due to swelling as a result of secondary ettringite formation. Under these conditions, then, the definition of 0.1% expansion at 20 days as “unacceptable behaviour” is shaky, at best, because the swelling component due to water ingress will vary from concrete to concrete independent of whether secondary ettringite forms.

After criticism by ASTM committee C09.02.02, Duggan & Scott [92] redefined the zero datum as the length of the saturated core before the start of the test regime (see Figure 7.6). This new zero was also used by Gillott et al [110, 111] in their experiments. This is a better approach because it attempts to remove the component of swelling vs time that is due to water uptake only. The rationale behind this definition is that the swelling due to water uptake after 3rd drying is equal to the total shrinkage that occurs between point A and point B (Figure 7.6c). This new definition led Duggan & Scott to define a new Pass/Fail limit of 0.05% at 20 days, rather than 0.1%.

This is, however, still not correct because during the Duggan régime the cores undergo a significant amount of permanent deformation. In the example shown in Figure 7.6 this amounts to 0.01 to 0.02% (compare point A with the 1st and 2nd resaturation points). It is well known that most permanent (irrecoverable) deformation in concrete that is subjected to shrinkage/swelling régimes occurs during the first cycle; shrinkage and swelling deformation during subsequent cycles
Table 7.1
Analysis of Strains During Duggan Test (data from ref. 92)

<table>
<thead>
<tr>
<th>Type of concrete tested</th>
<th>% strains observed</th>
<th>Expansion @ 20 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Non-reactive agg., low alk. cement</td>
<td>-0.067</td>
<td>0.046</td>
</tr>
<tr>
<td>B: Non-reactive agg., silica fume</td>
<td>-0.065</td>
<td>0.055</td>
</tr>
<tr>
<td>C: Non-reactive agg., silica fume, repeat</td>
<td>-0.051</td>
<td>0.045</td>
</tr>
<tr>
<td>D: Non-reactive agg., low alk. cement</td>
<td>-0.021</td>
<td>0.015</td>
</tr>
<tr>
<td>E: Expansive conc., failed in service</td>
<td>-0.084</td>
<td>0.080</td>
</tr>
<tr>
<td>F: Non-reactive agg., high alk. cement</td>
<td>-0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>G: Reactive agg. #1, low-alkali cement</td>
<td>-0.020</td>
<td>0.016</td>
</tr>
<tr>
<td>H: Reactive agg. #2, low-alkali cement</td>
<td>-0.056</td>
<td>0.062</td>
</tr>
</tbody>
</table>

Averages: -0.052, 0.046, -0.052, 0.055, -0.002, -0.054, 0.143, 0.087, 0.088

Figure 7.9
Comparison of 20 day Expansions Using Three Zero Definitions
are then approximately constant. Therefore, a more correct estimate of water-swelling after the 3rd drying cycle is the swelling that occurs between the 2nd drying point (point C) and the 2nd re-saturation point (point D).

Results reported by Duggan & Scott [92] were used to compare the effect of the three definitions of the zero point on the deformation at 20 days. The extracted data and analysis are shown in Table 7.1 and Figure 7.9. The zero data are defined as:

- Z1: Initial Duggan Zero, point B, Figure 7.6
- Z3: Revised Zero = Z1 - estimate of water swelling (pt D-pt C)

It should be noted that Attiogbe et al [12] also attempt to compensate for the water-swelling component of deformation by defining the zero point two days after the last heat cycle (see Figure 7.6). The disadvantage of this definition is that strains over the first two days that are, in fact, due to internal chemical reactions and expansion will not be measured.

The use of the revised zero, or any other zero, and definition of pass/fail criteria based upon absolute deformation values is not the best approach for two reasons:

- Regardless of the zero datum that is used, there must still be some uncertainty in the meaning of a given deformation at, say, 20 days. This uncertainty occurs because we cannot precisely differentiate between deformation caused by water-swelling and deformation caused by secondary expansions.
- A single point criterion is proposed to describe a time-dependent rate process — be it aar or secondary ettringite formation. Any number of reaction mechanisms could be envis-aged which pass through the proposed window of, say; between 0 and 0.05% expansion at 28 days. A single point criterion is not satisfactory.

A much more rational, and still simple, approach is one which can be developed from the work of Gillott et al [110]. Gillott calculates rates of expansion over two time periods, among others — i.e. from 3-22 days and from 22-90 days. He also defines a ratio of deformation rates = rate (3-22) / rate (22-90).

It is suggested that if the Duggan test is to be developed into a standard test method, then definition of pass/fail criteria along the lines of “rate of deformation” must be used. There are three distinct advantages:

- The expansion processes involved are rate processes and therefore the use of rate criteria are fundamentally valid
- The use of rates of deformation to define pass/fail eliminates the uncertainty associated with having to differentiate between water-swelling and other types of swelling. Duggan and Scott [92] indicate that the time-dependence of wetting-swelling is effectively complete 8 hours after the start of soaking. Thus, rates of deformation determined after this eight hour period should be related to the extent and consequences of secondary ettringite formation.
- Comparison of rates of deformation over different time periods (e.g. 3-22 days and 22-90 days) allows a rapid determination of whether the time-dependent process is accelerating or decelerating. A single deformation-time criterion as proposed by Duggan & Scott cannot do this.
Chapter 8
General Discussion

A review of case studies indicates that deterioration of concrete is usually a result of a combination of effects. Alkali-aggregate reaction, corrosion and sulphate attack appear to be principal mechanisms. Some case studies indicate that secondary ettringite formation may also be a principal mechanism for some types of concrete. The number of cases that can be directly related to secondary ettringite formation is small; however, a detailed review of research in the area combined with a few simple deductions indicate that the rate of incidents that can be wholly or partially attributed to secondary ettringite formation will increase.

The main question posed at the beginning of this report was: is there, or is there likely to be, a potential secondary ettringite formation problem in North America? Examination of the available literature does not reveal any incident of deterioration in North America directly attributed to secondary ettringite formation. Therefore, one conclusion based on this review is that there is not presently a secondary ettringite problem in North America.

However, good quality laboratory research confirms that secondary ettringite formation can produce expansion and cracking of heat-treated concrete made with North American commercial cements. In North America it is not unusual to find Type 30 cements with SO$_3$ contents in the range 3.5 to 4.0% — and could be as high as 4.5%. It is not unusual to find alumina contents of 5% or more and C$_3$A contents of 9% or more. Calculation of the S/A or S$_2$/A ratios for such cements places them in the maximum expansion ranges determined by Heinz and Ludwig and by Gillott.

Cement with high sulphate and alumina contents results in the potential for production of a large quantity of ettringite and thus high potential expansion. The high Blaines currently used for Type 30 cements results in a heterogeneous microstructure, easier ion transport to nucleation sites and requires even higher sulphate contents to prevent rapid set.

The presence of cement, aggregate and steel together in concrete result in a weak interfacial region which has high calcium hydroxide content, with orientated crystals, high in porosity and high in ettringite content. This is also the region that cracks when excessive heat treatment is applied.

On the concrete production side, the author is aware of concrete treated with maximum temperatures in the range 60-70°C and delay periods in the range 1-3 hours. Furthermore, some production processes using high heating and cooling rates (as high as 25-30°C/hr) have been observed. A 70°C maximum temperature is within the range where ettringite starts to decompose and sulphates integrate into the structure of calcium silicate hydrate; research indicates that sulphate in this form can slowly re-enter the pore solution at a later age, and react with aluminates to produce secondary ettringite. The potential inadequate delay periods and excessive heating and cooling rates could damage the concrete to provide sufficient nucleation sites for secondary ettringite formation and destruction.

In Canada we often have precast concrete that is subjected to frequent wetting and drying and freezing and thawing cycles; cycles which will exacerbate any potential secondary ettringite problem. Fortunately, much of the concrete is also air-entrained, which appears to result in substantial dampening of the secondary-ettringite deterioration process.

The conclusion is that given current cement production and construction practices there does appear to be a potential for a secondary ettringite formation problem in North America.

Possible remedies in the cement plant are to strive towards the reduction of C$_3$A, SO$_3$ and the finenesses of cements used by the precast industry. Better test methods need to be developed to evaluate the potential long-term stability of cements in concrete.
The precast concrete industry should strive towards more stringent specifications. It is suggested that the new German specifications may be appropriate for consideration by North American authorities. There is substantial evidence that air-entrainment, pozzolans and limestone aggregate can all contribute towards reducing the potential for secondary ettringite formation.

Much more research is also necessary. Much of past research has been performed on commercial cements. Clearly, to determine the conditions under which secondary ettringite forms, and thus to propose more precise specifications, we need to perform careful experiments on specially prepared cements - cements where cement composition, gypsum content, fineness, and other factors are strictly controlled. At the same time, experiments on commercial cements should also continue in order to provide relevance to the results from the controlled experiments.

The development of adequate test methods to evaluate long-term durability is also a crucial theme for future research. It is unfortunate that the Duggan test started out on a poor footing — lack of proper attention to detail and lack of control during early experiments severely limited the significance of the early findings. More careful research by Gillott, however, and realization that some improvements to the test method can still be made suggest that a future variation of the Duggan test may prove to be a useful practical test method, and one that could be developed into an accurate standard test method.

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The contents of this report reflect the research and views of the author, who is responsible for the accuracy of the report. The opinions expressed and conclusions drawn in this report are not necessarily those of the Portland Cement Association.
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**METRIC CONVERSIONS**

Following are metric conversions of the measurements used in this text. They are based in most cases on the International System of Units (SI).

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Metric Conversion</th>
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</thead>
<tbody>
<tr>
<td>1 in.</td>
<td>= 25.40 mm</td>
</tr>
<tr>
<td>1 sq in.</td>
<td>= 645.16 mm²</td>
</tr>
<tr>
<td>1 ft</td>
<td>= 0.3048 m</td>
</tr>
<tr>
<td>1 sq ft</td>
<td>= 0.0929 m²</td>
</tr>
<tr>
<td>1 sq ft per gallon</td>
<td>= 0.0283 m³/L</td>
</tr>
<tr>
<td>1 gal</td>
<td>= 3.785 L</td>
</tr>
<tr>
<td>1 kip = 1000 lbf</td>
<td>= 4.448 kN</td>
</tr>
<tr>
<td>1 lb</td>
<td>= 0.4536 kg</td>
</tr>
<tr>
<td>1 lb per cubic yard</td>
<td>= 0.5933 kg/m³</td>
</tr>
<tr>
<td>1 psf</td>
<td>= 4.882 kg/m²</td>
</tr>
<tr>
<td>1 psid</td>
<td>= 0.006895 MPa</td>
</tr>
<tr>
<td>No. 4 sieve</td>
<td>= 4.75 mm</td>
</tr>
<tr>
<td>No. 200 sieve</td>
<td>= 75 μm</td>
</tr>
<tr>
<td>1 bag of cement (U.S.)</td>
<td>= 94 lb = 42.6 kg</td>
</tr>
<tr>
<td>1 bag of cement (Canadian)</td>
<td>= 88 lb = 40 kg</td>
</tr>
<tr>
<td>1 bag per cubic yard (U.S.)</td>
<td>= 55.8 kg/m²</td>
</tr>
<tr>
<td>deg. C</td>
<td>= (deg. F - 32)/1.8</td>
</tr>
</tbody>
</table>
SINOPSIS: Este reporte comprende una revisión y análisis de la literatura existente relacionada con las causas, los efectos y la prevención de la ettringita secundaria (retrasada) en el concreto. Se examinaron más de 300 publicaciones. Se tratan primeramente los estudios en los cuales el daño en el concreto posiblemente fue causado por la formación de ettringita secundaria. Posteriormente, se trata la investigación fundamental relacionada con la formación de la ettringita secundaria, su química y los mecanismos de formación. Se analizan as investigaciones más importantes sobre el tema. Asimismo, se determina la importancia potencial (a) del método de curado por calentamiento (b) de la química del cemento. En el último capítulo, se evalúa una prueba rápida sobre la evaluación de la susceptibilidad del potencial de la ettringita secundaria (ensaye de Duggan). El análisis indica que parece haber potencial en Norte America para la formación de ettringita secundaria; es muy probable que la formación de ettringita secundaria pueda llevar a un deterioro significativo del concreto tratado con calor. Sin embargo, es poco probable que la formación de ettringita secundaria pueda ser el único mecanismo responsable del deterioro prematuro. Los factores críticos que determinan la extensión del daño debido a la formación de ettringita secundaria, son: (a) la duración del periodo de retraso antes del calentado del concreto, (b) la severidad del régimen de calentado o enfriamiento, y (c) la relación $SO_4/AlO$, del cemento. No existe evidencia de que los concretos no tratados con calentamiento son susceptibles a este fenómeno. Mayor investigación y mejoras en el ensaye de Duggan puede resultar en el desarrollo de un método de prueba estándar para analizar la estabilidad y la durabilidad del concreto a largo plazo.


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