DELAYED ETTRINGITE FORMATION IN PORTLAND CEMENT PRODUCTS

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FOREWORD

The thesis is structured around a series of original papers and unpublished work on the subject of delayed ettringite formation. Chapters 1 and 2 follow the traditional format outlining the objectives and scope of the work and providing an extensive literature survey. The results of the original work are presented in chapters 3 to 8. Each chapter is a self-contained unit and contains a full description of the experimental work, results and conclusions specific to the particular problem investigated. Some repetition, particularly with reference to certain published work, is a consequence of this format selection. All chapters are linked as different aspects of the central problem are presented. A general summary of all the findings and major over-all conclusions are presented in chapter 9.

A list of papers (published and submitted) from this work follows.

1 Fu Yan, Xie P., Gu P. and Beaudoin J. J., "Significance of Pre-Existing Cracks on Nucleation of Secondary Ettringite in Steam Cured Cement Paste", *Cement and Concrete Research*, Vol. 24, No. 6, pp. 1015-1024, (1994).

2 Fu Yan, Xie P., Gu P. and Beaudoin J. J., "Preferred Nucleation of Secondary Ettringite in Pre-Existing Cracks of Steam-Cured Cement Paste", *Journal of Materials Science Letters*, Vol. 12, pp. 1864-1865, (1993).

3 Fu Yan, Gu P., Xie P., and Beaudoin J. J., "Application of Secondary Ettringite formation in Steam-Cured Expansive Cement to Friction Pile Technology", *Journal of Materials Science Letters*, Vol. 13, pp. 477-479, (1994).

4 Fu Yan, Gu P., Xie P. and Beaudoin J. J., "Kinetic Study of Delayed Ettringite Formation in Hydrated Portland Cement Paste", *Cement and Concrete Research*, Vol. 25, No. 1, pp. 63-70, (1994).

5 Fu Yan, Gu P., Xie P. and Beaudoin J. J., "Effect of Temperature on Sulphate Absorption/Desorption by Tricalcium Silicate Hydrates: an internal sulphate source for delayed ettringite formation", *Cement and Concrete Research*, Vol. 24, No. 8, pp. 1428-1432, (1994).

6 Fu Yan and Beaudoin J. J., "A Through Solution Mechanism for Delayed Ettringite Formation in Pre-Existing Cracks in Portland Cement Mortar", *Journal of Materials Science Letters*, Vol. 14, pp. 217-219, (1995).

7 Fu Yan and Beaudoin J. J., "Mechanisms of Delayed Ettringite Formation in Portland Cement Systems", Accepted for publication in ACI Material J., (1995).

8 Fu Yan and Beaudoin J. J., "Mechanisms of Delayed Ettringite Formation in Portland Cement Systems", Presented at *Cement & Concrete Science Symposium*, St. Annes College, Oxford, UK, 26-27 September, (1994).

9 Fu Yan, Ding J. and Beaudoin J. J., "Deterioration of portland cement products due to delayed and secondary ettringite formation", Accepted for publication in Proc. of Fourth CANMET/ACI Intl. Conf. on Durability of Concrete, Sydney, Australia, August 17-22, (1997).

10 Fu Yan and Beaudoin J. J., "Microcracking as a precursor to delayed ettringite formation in cement systems", submitted to *Cement and Concrete research* for publication, (1996).

11 Fu Yan and Beaudoin J. J., "On the distinction between delayed and secondary ettringite formation in concrete", Accepted for publication in *Cement and Concrete research*, (1996).

ABSTRACT

The thesis presents the results of an extensive research program on the deterioration of Portland cement concrete due to delayed ettringite formation (DEF). The study focuses on three aspects: (i) the mechanisms of DEF; (ii) a test method to determine the DEF potential of a given cement; (iii) some preventive measures to reduce the deterioration of portland cement products due to DEF.

The research work indicates that C-S-H gel will adsorb sulfate fast at high temperature resulting in quick depletion of the gypsum phase in the portland cement-water system. Sulphate adsorbed at high temperature is desorbed more slowly than that adsorbed at normal temperatures. Slower release of sulfate from an internal sulfate source may be a critical condition for DEF in high temperature cured Portland cement paste. Nucleation of a crystal requires less surface energy in a crack than in the cement paste matrix. Sulfate ions, after release from the C-S-H gel, will diffuse into the nearest microcrack and react with the Al-bearing materials in the crack to nucleate and crystallize ettringite. Growth of ettringite crystals opens the crack and damages the cement products.

A test method to determine the expansion potential, due to delayed ettringite formation (DEF), of portland cements initially moist-cured at high temperatures was developed. Expansion of cement mortars made with eight different portland cements was investigated. Different test parameters, such as, curing temperature, type of sand, sand/cement ratio, specimen size and pre-treatment, were studied to select the optimal test conditions and procedures. Expansion/time criteria to evaluate the DEF potential of a given cement from the results of this test method are discussed.

Siliceous materials can be used in portland cement products to reduce or eliminate deterioration due to DEF. Different siliceous materials have different characteristics relevant to the reduction of the deleterious expansion. The granulated blast-furnace slag, ggbs, and Class F fly ash are more effective in reducing the DEF expansion than Class C fly ash, silica fume and natural zeolite. The expansion of the mortar containing a siliceous material appears to be much delayed. Therefore long-term expansion should be considered in the selection of a siliceous material for use in a DEF-suspect cement. Microcracks play an important role in the expansion due to DEF. Control of microcracks using wollastonite micro-fibres should reduce the expansion of a DEF-suspect cement mortar.

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Table Captions

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NOTATION*

A ..... Al_2O_3;

AFm ..... $C_3A{\cdot}CaSO_4{\cdot}12H_2O$

AFt ..... $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$

C ..... CaO;

CH ..... $Ca(OH)_2$;

DEF ..... Delayed ettringite formation;

EDXA ..... Energy dispersive x-ray analysis;

FA ..... Fly ash;

ggbs ..... ground granulated blast-furnace slag;

H ..... H_2O;

HAC ..... High alumina cement;

H-HAC ..... Pre-hydrated high alumina cement;

NZ ..... Natural zeolite;

S ..... SiO_2;

SEF ..... Secondary ettringite formation;

SEM ..... Scanning electron microscopy;

SF ..... Silica fume

SM ..... Siliceous material(s);

XRD ..... X-ray diffraction;

* - Mineralogical notation, customary in cement science is used throughout the thesis.

Chapter 1

INTRODUCTION

- Background
- Objectives
- Scope

§ 1.1. Background

Ettringite (commonly referred to as the AFt phase) is a reaction product generally formed in the early stages of portland cement hydration. It occurs as a result of the hydration of the calcium aluminate phase in presence of calcium sulphate, e.g. gypsum. Ettringite subsequently converts to calcium aluminate monosulphate hydrate (the AFm phase) as excess calcium aluminate is normally present. Formation of ettringite at different times during the hydration of OPC can result in very different behaviours of OPC concrete products. Delayed ettringite formation has recently been recognized to be harmful resulting in cracking of the concrete products. Cases of concrete deterioration due to delayed ettringite formation have been reported mostly in Europe and USA.

Kennerley (1965) first reported the possibility of concrete damage due to 'secondary ettringite'* formation in the Roxburgh Dam, Otago, New Zealand. Case studies have since been mostly reported by European researchers. A group focussing on "the Research of Secondary Ettringite Formation in Portland Cement Concrete" was organized by the Canadian Standards Association Committee A5 (Hydraulic Cement) in 1991. The objective of this task group was to investigate the potential problems due to delayed ettringite formation in the Canadian concrete industry. Its purpose was to identify:

(i) The mechanism of delayed ettringite formation and its effect on concrete performance;

(ii) The constituents of concrete which may lead to damage by delayed ettringite formation;

(iii) The environmental parameters which may lead to damage of concrete by delayed ettringite formation;

* The terms delayed ettringite and secondary ettringite have been used interchangeally by many workers. This has caused considerable confusion and is incorrect. The distinction will be discussed in detail later.

(iv) The most suitable test method to predict the possibility of delayed ettringite formation.

The two terms "secondary ettringite formation (SEF)" and "delayed ettringite formation (DEF)" are often used and confused. They both occur in actual concretes under different conditions. A comparison of the SEF and DEF is provided in Table 1.1. The study presented in this thesis is focused on DEF.

Table 1.1. Comparison of DEF and SEF

	Type of Concretes	Causes	Ettringite Formation	Expansion Rates
DEF	Steam cured precast concrete products.	Sulphate adsorption in C-S-H gel during steam curing.	Sulphate slowly releases from C-S-H gel, migrates into cracks and reacts with local Al-bearing materials.	Relatively slow.
SEF	Any concrete member.	Calcium sulphate forms from decomposition of AFt or AFm phases by severe drying.	Calcium sulphate quickly dissolves upon re-wetting and sulphate migrates into cracks to react with local Al-bearing materials.	Relatively quick.

The potential for deterioration of Portland cement concrete due to delayed ettringite formation has been recognized in the precast concrete industry since Heinz et al reported cases related to high temperature (>75 °C) steam cured concrete (Heinz and Ludwig, 1987; Heinz, Ludwig and Rudiger, 1989). They argued that delayed expansion in the concrete was due to the transformation of metastable monosulphate to ettringite when steam curing was followed by normal temperature moist curing at later ages. Investigations of this phenomenon have recently been reported by many researchers (Siedel, Hempel and Hempel, 1993; Grabowski et al, 1992).

The reaction products of tricalcium aluminate in the presence of gypsum and lime, as in Portland cement hydration, include both monosulphate and tetracalcium aluminate hydrates. These hydrated aluminates are essential components for ettringite formation at later ages. The source of SO_3-bearing materials in presence of the aluminate phases appears to be critical for delayed ettringite formation. Mechanisms of sulphate

attack on concrete have been widely investigated. Ettringite-related deterioration of concrete in a sulphate-free environment remains unclear.

It has been recently reported (Brown and Bothe, 1993; Grusczscinski, Brown and Bothe, 1993) that ettringite is still formed at elevated temperatures; monosulphate was not observed by XRD. It would appear that another mechanism of supplying sulphate for secondary ettringite formation may exist. Some insight into this apparent controversy is provided in early research by Lerch et al. (1946, 1929). They found that some sulphate added to Portland cement in the form of gypsum could not be accounted for subsequent to hydration. They postulated that the sulphate could be bound by the C-S-H gel structure to form a new phase called "phase X". Kalousek and Adams (1951) argued that "phase X" was a gel containing all the oxide constituents of cement. It was transformed from a solid solution of sulphoaluminates in the temperature range 25 to 100 °C. The transformation rate clearly increased with an increase of temperature.

Odler (1980) reported that about 9.8% gypsum could be bound in hydrated C_3S. Similar results were obtained by Copeland et al (1967), Bentur (1976) and Mehta and co - workers (1979). Copeland et al. (1967) indicated that sulphate combined with C-S-H gel at early ages and was then released at later ages. They found that ettringite apparently formed without any external additions of sulphate indicating that the sulphate for secondary ettringite formation must come from the hydrated Portland cement itself. An increase of temperature accelerates the sulphate adsorption rate by Portland cement hydrates. Competition for gypsum exists between the C-S-H gel and the hydrating calcium aluminates at very early hydration ages. Taylor (1993) concluded that, although C-S-H gel was not directly involved in reactions leading to ettringite formation, it did affect the stability of ettringite through its ability to take up both sulphate and aluminate.

Other notable case studies (Pettifer and Nixon, 1980; Shayan and Quick, 1992) have been reported since Kennerley (1965) suggested the possibility of deterioration of

concrete by delayed ettringite formation. The investigations revealed that ettringite usually was present in cracks, voids and the transition zone at the aggregate-binder interface (Macleod and Hall, 1991). Tepponen and Erickson (1987) discussed the post-cracking behaviour of steam cured concrete (75-80 °C) railway sleepers, indicating that microcracks were the primary cause of deterioration. Sylla (1988) postulated that the initial cracks resulting in such deterioration might occur during thermal treatment. Monteiro, Gjorv and Mehta (1989) studied ettringite formation at the steel-paste interface. Highly concentrated ettringite crystals apparently existed in the transition zone. Pre-existing cracks in concrete appear to be an important factor in the deterioration of concrete when internal sulphate sources exist as mentioned above.

It can be inferred from crystal nucleation theory that there is a potential for preferred nucleation at a solid surface rather than in solution in order to lower the free energy of the newly formed system (Wylie, 1952). The candidates prior research based on this theory demonstrated the significance of pre-existing cracks on nucleation of secondary ettringite in steam cured cement paste. A recent study by Scrivener and Taylor (1993) appears to confirm this phenomenon. It was suggested that high temperature steam curing followed by high temperature drying to form microcracks was an optimum condition for concrete deterioration due to delayed ettringite formation. A theoretical analysis of the free energy change in the nucleation process was developed by the candidate from fundamental concepts and equations by Gibbs (1928) and Volmer (1939). The arguments supported the view that crystals preferentially nucleate in crack tip-zones rather than on plane solid surfaces. The effect of pre-existing crack size on crack propagation and expansion by secondary ettringite formation was also discussed in terms of Griffith fracture theory.

Two different arguments have been used to interpret ettringite related expansion mechanisms for Portland cement concrete: the crystal growth theory and the swelling

theory. Cohen (1982) postulated that expansion results from the growth of ettringite crystals formed on the surfaces of Al-bearing particles. The growth of these crystals results in crystallization pressure and expansion occurs. Mehta (1973) argued that expansion is attributed to the swelling of colloidal particles of ettringite. The formation of this swelling gel occurs by a through-solution mechanism. Expansion could occur either by intercalation or surface adsorption effects. The phenomenon of preferred nucleation of secondary ettringite in pre-existing cracks appears to support arguments for a through-solution deposition mechanism. The resulting expansion likely occurs through crystal growth in conformance with Cohen's postulation.

A rapid test method referred to as the Duggan Test has been reported by Grabowski et al. as relevant to detecting delayed ettringite formation. It involves measurements of expansion on thermally cycled (82 °C drying/21 °C re-wetting) concrete cores. The major cause of expansion measured in the test is believed to be due to delayed ettringite formation. This is challenged by the candidate. The associated mechanisms of concrete deterioration are still not clear.

Sulphate adsorption from internal sources in hydrating systems containing C_3S, C-S-H gel, hydrated Portland cement, and gypsum has been studied with respect to delayed ettringite formation. The influence of C_3A addition on sulphate desorption was also investigated. The research indicates that C-S-H gel will adsorb sulphate faster at high temperature resulting in quick depletion of the gypsum phase in C-S-H - gypsum mixtures. The critical temperature for sulphate adsorption by C-S-H gel is above 65 °C. Sulphate adsorbed at high temperature is desorbed more slowly than that adsorbed at normal temperature. Slower release of sulphate from an internal sulphate source may be a critical condition for delayed ettringite formation in high temperature cured Portland cement paste.

§ 1.2. Objectives and Scope

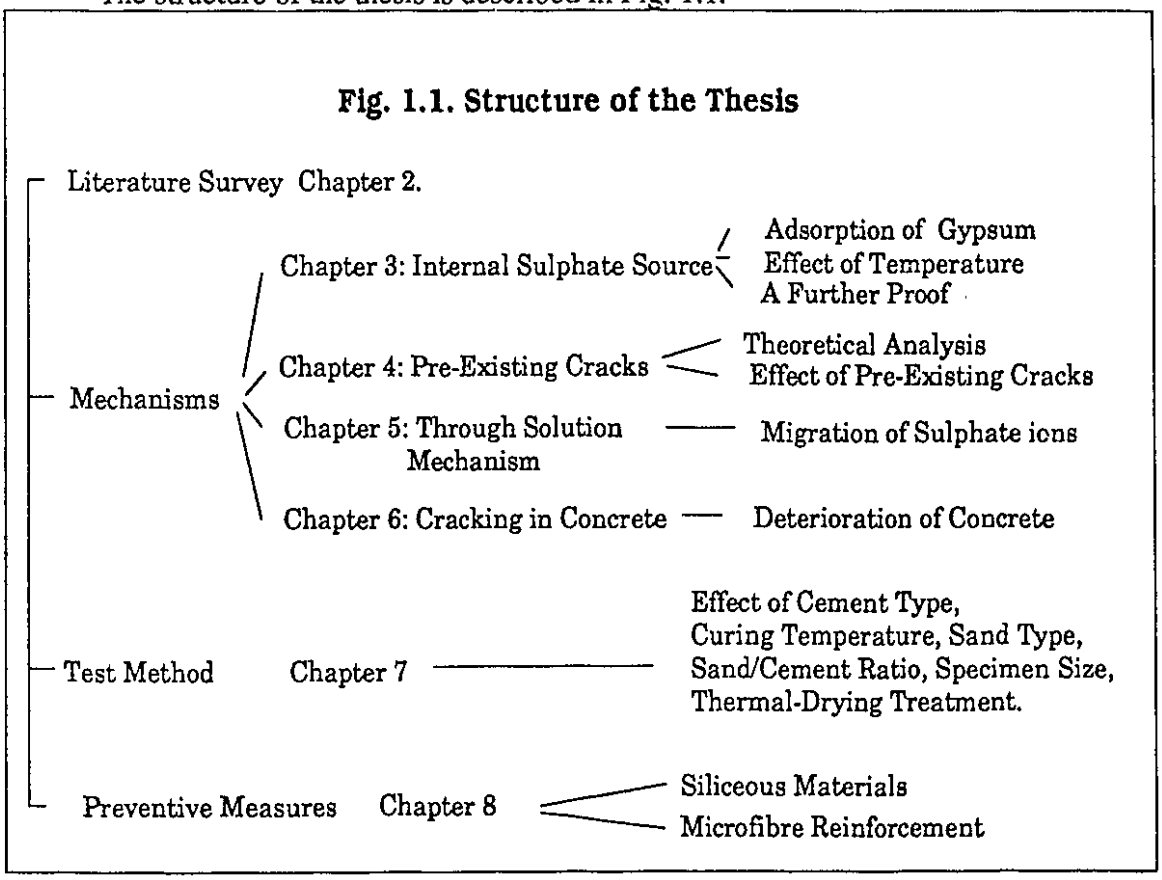
The objectives of this research are to clarify and delineate the mechanisms of delayed ettringite formation, and to provide the basis for suggesting measures of preventing its occurrence in Portland cement products.

The research will include work on the following aspects of delayed ettringite formation:

- Mechanisms of delayed ettringite formation in Portland cement products;
- Development of a rapid test to determine the potential for delayed ettringite formation in Portland cement products;
- Preventive measures for reducing or eliminating deterioration of Portland cement products due to delayed ettringite formation.

The structure of the thesis is described in Fig. 1.1.

Fig. 1.1. Structure of the Thesis



Chapter 2

LITERATURE SURVEY

- Crystallization of Calcium Sulphoaluminates
- Expansion due to Ettringite Formation
- Delayed Ettringite Formation (DEF)
- Case Studies

§ 2.1. Introduction

Delayed ettringite formation (DEF) has been considered as potentially affecting the durability of the concrete. Case studies indicating the significance of the research in this area have been mostly reported by European researchers. A focus group on "the Research of Secondary Ettringite Formation in Portland Cement Concrete" was organized by Canadian Standards Association Committee A5 (Hydraulic Cement) in 1991. The objective of that group was to investigate the possibility of DEF problems in the Canadian concrete industry. Emphasis was given to the following:

(1) Identification of the mechanism of secondary ettringite formation and its effect on concrete performance;

(2) Determination of the constituents of concrete which may lead to damage by secondary ettringite formation;

(3) Establishment of the environmental parameters which may lead to damage of concrete by secondary ettringite formation;

(4) Development of a test method to predict the possibility of secondary ettringite formation.

It is noted that the term "secondary ettringite formation" and " delayed ettringite formation" are often used interchangeably by various authors in the research publications. The terms usually represent the same thing if no identification further distinction is made. This has led to confusion and will be discussed later in the thesis.

Day (1992) published an extensive literature review including 327 references. Most of the references concerned the research of ettringite formation in general and related durability problems in cement and concretes systems. A few addressed the topic of DEF. Research on DEF is still primarily on a phenomenological level with respect to the deterioration of concrete. The mechanism, appropriate test methods and suitable preventive measures remain unclear.

This literature survey begins with a review of the theoretical analysis of ettringite crystallization discussed by many researchers.

§ 2.2. Crystallization of Calcium Sulphoaluminates

§ 2.2.1. The Crystal Structure of Calcium Sulphoaluminates

The natural mineral ettringite (Dana, 1932) was first reported in 1847 to occur in limestone minerals in Lava at Ettringen and Mayen in the Rheinland. Ettringite was considered to be a mineral consisting of minute, colorless, hexagonal crystals. The compound now widely accepted as having a formula of $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ was first observed in 1890 by Candlot (1890). It also occurs naturally as the mineral ettringite. McConnell and Murdoch (1962) reported that ettringite should have the general formula: $16[A_4(XO_4)_{23}\ (H_2O)_{12}]$, where "A" represents six-fold coordinated atoms (such as Ca, Na and Al), and "X" four-fold coordinated atoms (such as S, Si, H4 and Al).

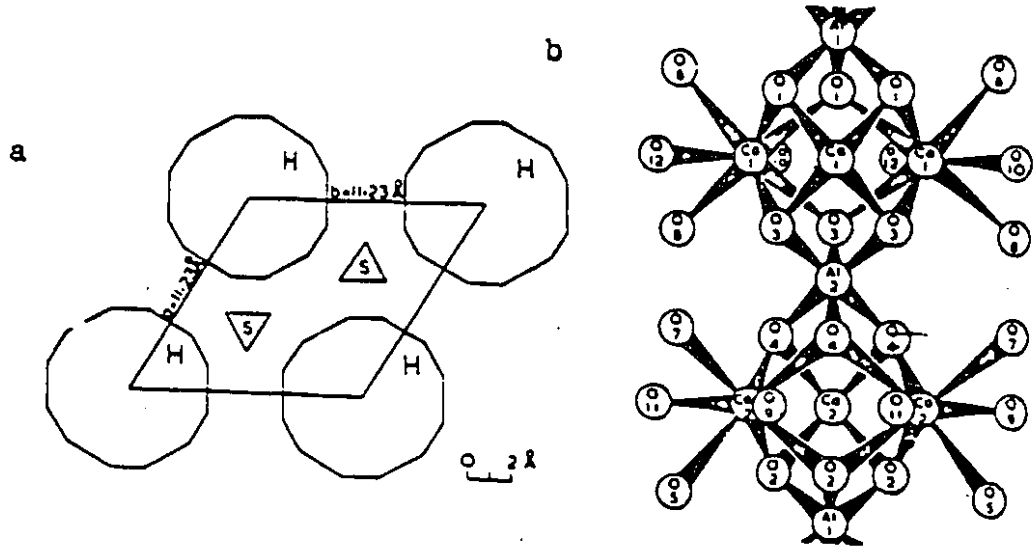


Fig. 2-1. Crystal structure of ettringite (Moore and Taylor, 1970).

Moore and Taylor (1970) described ettringite in a different way: and assigned it the following formula $Ca_6[Al(OH)_6]2(SO_4)_3$ $25.7H_2O$ (Fig. 2-1). They reported that the ettringite crystals are predominantly in the shape of hexagonal prisms which consist of columns and channels running parallel to the prism axis with SO_4-groups and H_2O molecules in the channels. The columns contain $\{Ca_6[Al(OH)_6]_2 \cdot 24H_2O\}^{6+}$. The channels contain $[(SO_4)32H_2O]^{6-}$ groups per half unit cell in each case. Each of the columns is a chain of alternating polyhedra - one of aluminium and three of calcium. A calcium atom is linked to four H_2O molecules and four OH-groups. A Ca polyhedron is shaped as a trigonal prism with two additional apices in which H_2O molecules [O(9)-O(12)] are located. H_2O molecules [O(5)-O(8)] are also at the two main apices of the trigonal prism. The remaining four main apices contain OH-groups [O(1)-O(4)] common to the Al polyhedra. The aluminium atom is linked to six OH-groups.

Taylor (1973) simplified the ettringite crystal structure into four positively charged columns in a trigonal structure. Anions and water molecules exist between them. The lattice dimensions in the a and b direction are 11.23 Å and 10.7 Å in the c direction. The anion group, usually sulphate, can be partially or completely replaced by others such as $CO^{3=}$, $CrO^{4=}$, Cl^-, and IO^{3-}; the metal group, usually aluminium, can be replaced by Ti, Cr, Mn, Fe and Ga and; the calcium can be replaced by strontium. Some minerals with parallel structures to the ettringite-group crystals might result from the replacement of foreign ions in the ettringite structure, for example: in thaumasite, silicon replaces aluminium in the columns, and in jouravskite, manganese replaces aluminium. For both of them, carbonate replaces the water molecules existing between the columns of the ettringite structure. Other research has indicated the possibility of the replacement of aluminium and sulphate by various foreign ions in ettringite structures [Lukas, Roeck and Hagleitner, (1977); Zhang, Zhou and Lou, (1980)]. Many oxyanions are believed to substitute for sulphate in the ettringite structure such as arsenate, borate, chromate,

molybdate, selenate and vanadate [Hassett, McCarthy, Kumarathasan and Pflughoeft-Hassett, (1990); Kumarathasan, McCarthy, Hassett and Pflughoeft-Hassett, (1990)]. The other compound closely related to ettringite is referred to as calcium, monosulphoaluminate with a formula of $C_3A{\cdot}CaSO_4{\cdot}13H_2O$. It has been known since 1929 [Lerch, Ashton and Bogue, (1929)]. This "low" form of sulphate and the "high" form of sulphate can convert to the other under different thermodynamic and chemical kinetic conditions.

§ 2.2.2. The Morphology of Ettringite

The morphology and crystal size of ettringite varies with the different conditions under which it forms. Most of the SEM observations show that ettringite is normally a slender, needle-like, crystal with prismatic hexagonal cross section [Schwiet, Lucwing and Jager, (1966); Midgley and Pettifer, (1971); Mehta, (1973); Mehta and Hu, (1978)]. Its size depends on water-cement ratio, that is , the effective space which ettringite is able to occupy [Mehta, (1969)]. It can grow up to 100 μ m long with a large enough w/c. The particle size of Al-bearing agents is also a main factor affecting the size of ettringite [Cohen, Campbell and Fowle, (1985)]. Large particles of Al-bearing agents form a large amount of small ettringite crystal and the period of expansion can last longer. Small particles will produce large size crystals quickly at an early stage because of the large surface area and fast reaction rate. The ettringite crystals will also be smaller in size in the presence of CH [Possetti, Chiocchil and Paolini, (1982)].

The form of ettringite is relevant to studies of the mechanism of expansion. Lerch et al. (1929) reported that the synthetic ettringite consists of long slender needles which often form sphere-like. Mehta (1976) also reported the presence of spherulite ettringite. Ogawa and Roy (1982) found that during the hydration, the ettringite is formed as very small irregular particles around Al-bearing particles in the early stages, and then changes

to long needle-like crystals arranged radially around the Al-bearing particles. This was considered as the start of expansion.

§ 2.2.3. The Stability of the Calcium Sulphoaluminates

The commonly accepted view that ettringite is more stable in sulphate solutions and lime water than in distilled water, and that monosulphate in solutions containing calcium sulphate, sodium sulphate, calcium chloride and sodium chloride may transform to ettringite is based on the work of Lerch, et al. (1929). This indicated that ettringite should be stable in a cement and concrete environment.

The effect of cement constituents on the stability of both ettringite and monosulphate has been widely studied by many researchers. Mehta (1969) noted that monosulphate may exist along with ettringite only if the solutions surrounding it has the lower concentration of sulphate than is usually required for the existence of ettringite. Jones (1939) reported that the three conditions for monosulphate stability in aqueous solution are high calcium content, low sulphate content and high temperature. It is evident that the alkali content will also affect the solubility of ettringite. Hampson and Bailey (1982) reported the effect of pH value of the pore solution on the morphology of sulphoaluminates It was concluded that at pH 11.5 to 11.8, sulphoaluminate forms as ettringite crystals and at pH 12.5 to 12.8, some non-crystalline materials may form with a composition similar to ettringite. The latter loses its characteristic fibrous morphology.

The stability of sulphoaluminate can also been determined by utilizing solubility product data. Zhang, et al (1980) reported that the solubility product of ettringite (1.0×10^{-40}) is much lower than that for monosulphate (1.7×10^{-28}), indicating that under ambient condition ettringite is more stable in a cement solution than monosulphate. Therefore monosulphate naturally has the tendency to form ettringite.

§ 2.2.4. Effect of Temperature

Several studies have demonstrated that the calcium sulphoaluminates are thermally-unstable phases. They transform from one state to the other with the change of curing temperature during which the sulphate-groups and water molecules are re-arranged in the structures. Monosulphate was reported to be a metastable phase in hardened cement paste [Kalousek, (1941)]. This was recently confirmed by Heinz and Ludwig (1989) and Klemm and Adams (1990). Monosulphate will preferentially form at steam curing temperatures above 70 °C and then transform to ettringite at later ages. Mchedlov-Petroysan's (1985) work suggested that ettringite can exist stably in cement paste at temperature up to about 70 °C; however above 70 °C monosulphate becomes the stable phase. Chino and Kawamura (1988) demonstrated an apparent decrease of ettringite content in cement pastes with an increase of temperature from 20 to 90 °C by X-ray diffraction analysis. Great change occurs at curing temperatures above 70 °C. Stadelman (1988) utilized DTA to show a clear diminishing of ettringite at temperatures above 60 °C and a corresponding increase of the monosulphate peaks. He then found that the ettringite peaks reformed after certain periods of moist curing and noted a corresponding concrete expansion.

Some controversies concerning a critical temperature resulting in the unstable ettringite-monosulphate transformation have been well documented by many researchers. Mehta (1972) indicated that ettringite can be found in cement paste subjected to a 65 °C drying condition and that the decomposition starts when drying occurs at 93 °C. He also noted that no apparent decomposition of ettringite occurs at 93 °C under moist conditions. The ettringite that was exposed to moisture began to decompose at 149 °C. Other research has also shown the similar results. It has also been reported that ettringite can exist stably in aqueous solution up to 93 °C [Satava and Veprek, (1975)].

One explanation for the transformation of sulphoaluminates was first postulated by Kalousek (1965). He believed that the depletion of ettringite at high temperature can be attributed to the substitution of sulphate ions in the structure of C-S-H gel , e.g. tobermorite, resulting in the loss of sufficient sulphate for the stable existence of ettringite. It was shown that the amount of missing SO_3 clearly increased with the rise of temperature from 24 to 82 °C. Correspondingly the decrease in amount of ettringite was accompanied by an increase of monosulphate. Kalousek suggested that the missing SO_3 might be the source of DEF. The missing SO_3 was suspected to be associated with the C-S-H gel structure. It could not be found in the form of ettringite and monosulphate at high temperature. No further reports were published to validate the arguments experimentally.

Ettringite can quickly lose its water when dried at a temperature higher than 70 °C. A greater loss was demonstrated by Abo-El-Enein et al. (1984) who reported that ettringite formed at 25 °C loses about 20 water molecules after drying at 58 °C. Ghorab et al. (1980) also reported that ettringite can be destroyed by drying at 74 °C.

§ 2.2.5. Effect of Alkali

The action of alkali is believed mainly to affect the solubilities of reactants (e.g. C_3A, CH and CSH_2) in the C_3A - CSH_2 - CH - H_2O system and hence the concentrations of dissolved ions (e.g. OH^-, $SO_4^=$, Ca^{++}, etc.). Wang et al. (1986) presented the results that alkali could apparently increase the solubility of ettringite and decrease that of calcium hydroxide. The OH^- concentration in pore solution containing alkali would be 15 times as high as that without alkali. The presence of alkalis greatly suppressed the dissolution of CH but enhanced the ettringite formation. Ettringite was able to form in an alkaline solution at pH of 13.3 at normal temperatures and at alkali concentration as low as 0.08M. Ettringite became unstable and started to decompose at higher temperature (60

°C) or higher alkali concentration (0.2 to 1.0M). Ghorab and Abou El Fetouh (1986) reported that at higher alkali concentration monosulphate appeared more stable.

Another approach was studied by Chino and Kawamura (1988) postulating that the presence of alkali would reduce or decompose ettringite due to the following reaction $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O + 6NaOH \longrightarrow 3NaSO_4 + 4Ca(OH)_2 + 2Al(OH)_3$. In this system $SO_4^=$ was believed to be more stable in sodium sulphate than in ettringite.

§ 2.2.6. Effect of Carbonation

Carbonation of ettringite related systems has been widely studied. Taylor (1990) pointed out that carbonation during the ettringite formation process could result in the formation of thaumasite ($\{Ca_6{\cdot}[Si(OH)_6]_2{\cdot}24H_2O\}{\cdot}[(SO_4)_2]{\cdot}[(CO_3)_2]\}$), and cause the deterioration of cement or concrete. He indicated that thaumasite could easily be misidentified as ettringite. Thaumasite is more stable than ettringite at low temperatures (< 4°C) and high relative humidity. With a proper supply of sulphate and carbon dioxide, ettringite might transform to thaumasite. Taylor noted that thaumasite cannot form directly and usually forms from ettringite. He believed that this transformation could contribute to the destruction of cement paste or concrete. These conclusions are partially supported by Ludwig and Mehr (1986) from their investigations. The decomposition of ettringite to thaumasite was mainly found to occur after long-term cold curing (< 20 °C). No information proved that thaumasite will cause expansion. Sylla (1988) found some evidence indicating that expansion can be attributed to both ettringite and thaumasite. His specimens were steam-cured at 80 °C and then stored at 5 °C with CO_2 present. A high content of thaumasite was apparently found along with ettringite. Case studies related to concrete deterioration due to thaumasite formation have been reported in UK (Crammond and Halliwell, 1995) and Canada (Bickley et al. 1993).

The carbonation of monosulphate to produce ettringite and hemicarbonate was first noted by Seligmann and Greening (1968). More recent work by Kuzel and

Strohbouch (1989) indicated that CO_2 acted as a catalyst to provide a favorable environment in Portland cement concrete for monosulphate transformation to ettringite. Klemm and Adams (1990) reported that a carboaluminate reaction product also had two forms comparable to the AFt and AFm sulphoaluminate phases. The AFt analogue appeared much less stable than the AFm analogue in a portland cement concrete environment. Carboaluminate and ettringite could co-exist. It was emphasized that because of the slow reaction involved, DEF would occur. This corresponded with the deterioration of cement paste or concrete in which carbon dioxide or calcite existed.

§ 2.3. Expansion due to Ettringite Formation

§ 2.3.1. Expansion Theories

Cohen (1983) in an extensive review grouped the various theories on the expansion mechanisms of expansive cement into two schools of thought: one subscribing to the crystal growth theory and the other to the swelling gel theory. A brief summary of the theories ascribed to various authors is presented as follows:

Mehta's Swelling Theory

Expansion is the result of the swelling of ettringite colloidal particles. These gel-like particles have a large specific surface area analogous to C-S-H gel, and adsorb water resulting in cause overall expansion. The formation of this swelling gel occurs by a through-solution mechanism due to reaction between the expansive particles and the surrounding solution [Mehta, (1973)].

Cohen's Crystal Growth Theory

Expansion is the result of the growth of ettringite crystals forming on the surfaces of the Al-bearing particles and in solution. The growth of these crystals causes expansion through generation of crystallization pressure in regions of limited space [Cohen, (1982)].

Richards and Helmuth's Dense Coating Theory

A dense ettringite coating is formed on the surfaces of the Al-bearing particles during hydration. The layer grows filling the surrounding space. Space limitations result in particles being pushed apart and overall expansion [Richards and Helmuth, (1977)].

Ogawa and Roy's Loose Coating Theory

Expansion is dependent on the shape and orientation of ettringite particles. Very small particles of ettringite form around Al-bearing particles in the early stages of hydration. Then these particles form loosely networked needle-like crystals radially around Al-bearing particles. Expansion starts and causes expansion pressure after the reaction zones intersect [Ogawa and Roy, (1982)].

Polivka's Kinetics of Ettringite Formation Theory

Expansion due to ettringite crystals is dependent on the rate of formation. The magnitude of expansion in the early stages will be small when the ettringite crystals grow quickly, because the structure of cement paste has not hardened enough to facilitate expansion. The expansion will be relatively larger if the ettringite crystals form late after the cement paste gets considerable hardness [Aroni, Polivka and Bresler, (1966)].

Bentur and Ish-Shalom's Critical Hydration Theory

Further hydration of expansive particles after the first contact is formed can cause expansion at this critical degree of hydration. The time for the ettringite crystals to exceed the physical limitation of the surrounding space corresponds to the time at which critical hydration occurs [Bentur and Ish-Shalom, (1974)].

Budnikov and Kravchenko's Crystallization Nuclei Theory

The concentration of crystallization nuclei and the rate of growth of the ettringite crystals are the two critical requirements for the expansion. A large number of crystallization nuclei in the cement paste may cause a small expansion, if the reaction

rate is high. However, a small number of nuclei in the cement paste with a lower rate of crystal growth can produce a large expansion [Budnikov and Kravchenko, (1968)].

§ 2.3.2. Factors Influencing Ettringite Formation and Crystal Size

§ 2.3.2.1. Al-bearing Agent

C_3A, Tricalcium aluminate, is the major Al-bearing agent in Portland cement required for ettringite formation. Cohen and Mobasher (1991) studied the effects of Al-bearing agents on expansion time and indicated that there was an optimum content which could induce an appropriate amount of compressive stress in restrained concrete within a given expansion time.

§ 2.3.2.2. SO_3-bearing Agents

The SO_3-bearing agents can be divided into three types: hemihydrate ($CaSO_4 \cdot ½H2O$), gypsum ($CaSO_4 \cdot 2H_2O$) and anhydride ($CaSO_4$). Although hemihydrate will quickly hydrate to gypsum within 30 minutes after addition of water, Timusk and Sheikh (1977) observed that hemihydrate could delay expansion of their cement for several hours and result in a final larger expansion than gypsum.

Cohen and Mobasher (1991) reported that the relationship between total sulphate content and expansion time depended on the size and distribution of the Al-bearing agent particles. Generally, for expansive cement pastes, holding the amount of Al-bearing agent constant and increasing the sulphate content of the hydration system will result in an increase of the expansion period. The increase is almost linear for monosize Al-bearing agent particles and curvilinear for the polysize particles. Cohen's expansive cements model [Cohen, (1983)] also indicated that the expansion time is directly proportional to the amount of sulphate used.

§ 2.3.2.3. $Ca(OH)_2$ Content

Both the Crystal Growth Theory [Cohen. and Richards, (1982)] and the Swelling Gel Theory [Mehta, (1973)] agree that the presence of CH increases expansion. A major

difference between the two theories however is that according to the first, hydration is more favorable and quicker in the presence of lime and the mode of formation of ettringite is topochemical. According to the second theory, ettringite always forms by a through-solution mechanism, regardless of the presence or absence of lime. Further, unlike the first theory, the rate of hydration of the expansive particles is believed to be smaller in the presence of lime.

Nakagawa et al.'s (1990) test results indicated that in the absence of CH, no expansion was produced even though ettringite was formed. In this reaction, when Ca^{2+} ions are relatively scarce, ettringite forms as large crystals in solution. Ettringite can form either on the surface of Al-bearing particles or in solution. In the case of $C_4A_3\bar{S}$ alone, AFm and $Al(OH)_3$ are produced. This causes ettringite to crystallize from solution. $C_4A_3\bar{S}$ hydrates quickly in the presence of lime and becomes covered with a fine coating of ettringite crystals without changing the outer shape of the grain. The coating then begins to expand.

Possetti et al. (1982) found that in the presence of lime, as soon as the mixture had been completely converted into ettringite, a strong decrease of the SO_4^{-2} ion concentration in the contact solution occurred. This decrease corresponded to a considerable increase in the zeta potential of the particles, thus leading to further expansion. The increase in zeta potential of the ettringite in the absence of CH in solution was very small or practically zero. Further expansion did not take place.

§ 2.3.2.4. Particle Size

Cohen (1983) studied the effect of particle size on ettringite formation and expansion, and developed a model to explain the mechanism and kinetics of the expansion process in expansive cements. This model indicated that an increase in particle size of the Al-bearing agents increased the maximum length of a single ettringite crystal and the expansion time, but decreased the total number of ettringite crystals formed.

Richards and Helmuth's theoretical model (1977) showed that there was an optimum range of expansive particle size which gave the highest expansion. This optimum range was calculated to be 6.8 to 11 μ m. Particles above or below this size range produce less expansion or none at all.

§ 2.3.2.5. Effect of W/C

Mehta (1976) reported that large ettringite crystals could form in high w/c pastes, while small crystals formed in low w/c pastes. Budnikov and Kravchenko's Crystallization Nuclei Theory (1968) and Bentur and Ish-Shalom's Critical Hydration Theory (1974) indicated that fewer but larger ettringite crystals contributed less to expansion than a larger number of small crystals. Polivka's volume increase theory [Aroni, Polivka and Bresler, (1966)]. showed that in the high w/c expansive concretes, a large amount of ettringite formed in the pores which did not result in expansion of the concrete.

§ 2.3.2.6. Effect of Restraint

Ish-Shalom and Bentur (1975) studied the effects of various kinds of restraint conditions on expansion. Their model focused on the stage when the expanding individual spheres contacted each other (Fig. 2-2). Further expansion of these spheres gave rise to isotopic expansion if there was no restraint. This unrestrained condition could only exist at the top of the drilled shafts. The preferred direction of expansion under uniaxial restraint was perpendicular to that of the restraint forces causing distortion of the spherical particles. Under triaxial restraint, the only possible direction of ettringite growth was into the large pores between the spheres leading to self-densification of the material. This phenomenon might occur in the early stages of the expansive cement hydration in the lower part of drilled shafts. Another restraint condition was termed "hydrostatic restraint". This case happened in the later stages of hydration when the matrix had gained sufficient strength to isolate the expansive particles and to suppress the

ettringite growth into voids in the matrix. The only possible space for the ettringite formation was within the expansive particles themselves. The self-improvement of the material by this mechanism could, in the long term, result in a very high density and compressive strength.

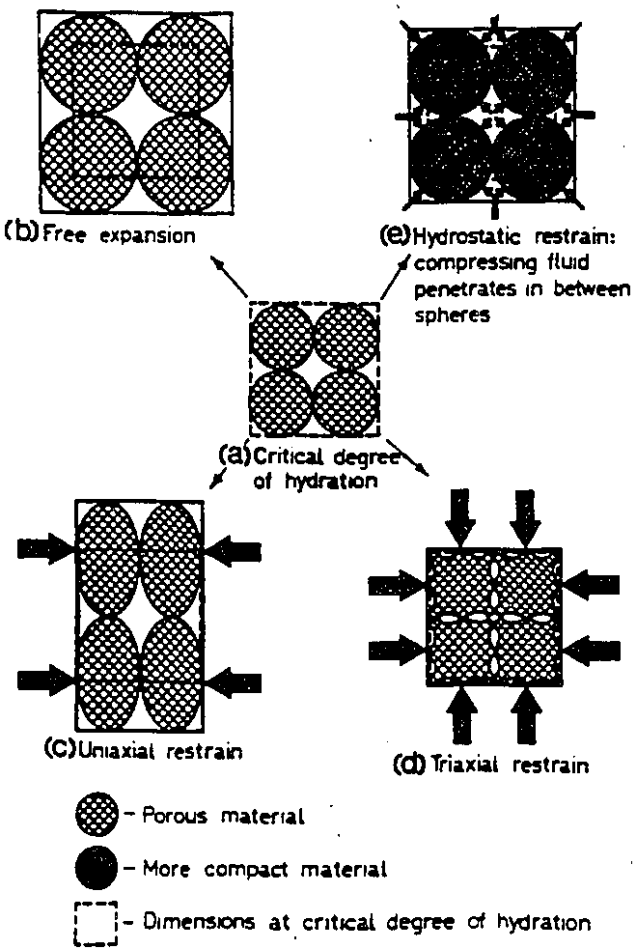


Fig. 2-2. Schematic representation of the structure of pure expansive component past (Ish-shalom and Bentur, 1975)

Lobo and Cohen (1991) also investigated the effect of restraint on the microstructure of expansive concrete using mercury intrusion porosimetry. The porosimetry results confirmed that restraint of expansive cement paste had the potential to improve its engineering and service properties by shifting its pore size distribution to a smaller size.

Although the effect of the restraint force on limiting the expansion of expansive concrete tends to vary with different test materials and test conditions, it was concluded by most researchers that some expansion still takes place under the most severe restraint conditions.

§ 2.4. Delayed Ettringite Formation (DEF)

Although AAR and DEF are two independent phenomenon, many case studies indicated that they are often function simultaneously in concrete [Johansen, Thaulow and Skalny (1993)]. Oberholster et al. (1992) reported that DEF is only found coupled with AAR in South Africa railway ties. Shayan and Quick (1992) suggested that since high temperature curing accelerates AAR, AAR is the primary cause of damage of railway ties, and DEF may play a secondary role filling in the cracks created by AAR at later ages. Diamond, Ong and Bonen (1994) believed that the primary ettringite generated during the pre-steaming hydration period was destroyed during the steam curing cycles and secondary ettringite forms within the paste matrix and deposits in cracks only when AAR has been present.

Although the mechanism of concrete deterioration due to DEF is still not clear, some key conditions required to induce DEF have been identified from case studies and laboratory tests. Knowledge of these conditions have benefited the precast concrete industry to factor affecting potential long-term damage. Day (1992) cited that there are three conditions leading to DEF (Hill, 1990):

(1) Use of portland cement having a high SO_3/Al_2O_3 ratio and high alkali content;

(2) Use of high curing temperature;

(3) Exposure to moisture.

§ 2.4.1. Constituents of Portland Cement

Glasser, Domidot and Atkins (1995) established some phase relationships and mass balances in the system $CaO\text{-}Al_2O_3\text{-}CaSO_4\text{-}Na_2O\text{-}H_2O$ to explain the DEF. They postulated that slow transformation of AFm, preferentially formed at high temperature, induces a swelling pressure within cement paste leading to its expansion as AFm reverts to the more stable AFt. Reactions involving gypsum, the most critical component of portland cement DEF, have been widely studied since Portland cement was commercialized. The content of gypsum in terms of SO_3 percentage is dependent on (1) the retardation process; (2) early strength requirement; and (3) volume stability. Brown (1965) indicated that the maximum strength could be obtained in steam-cured cement with an SO_3 content of 7.1%, but he noted such cement would result in high expansion. A content of 5-6% SO_3 in portland cement was suggested as a compromise.

Some studies have shown that the SO_3/Al_2O_3 ratio plays an important role in the reaction of DEF [Heinz and Ludwig, (1987)]. Other work has indicated that the expansion due to DEF depends mainly on the C_3A and SO_3 content in cement and not on the SO_3/Al_2O_3 ratio [Odler and Chen, (1995)]. An SO_3 content higher than 3.5% for Type 30 high early strength cement is allowed and the CA content is less than or equal to 7.5%. An SO_3 content greater than 4.5% can also be used in some cements passing the following test. The test requires that standard mortar bars soaked in water for 14 days have an expansion value less than 0.02%. This test has been questioned for evaluation of the possibility of DEF. Lerch and Ford (1948) reported results that some specimens exhibiting expansion less than 0.02% at 14 days can have significantly higher expansion

five years later. Siedel, Hempel and Hempel (1993) reported that no expansion due DEF is found in a concrete made with a PZ 45 cement (a Germany equivalent to Type 10 cement in Canada).

§ 2.4.2. Curing Temperature

DEF is primarily a result of the application of relatively high curing temperatures. The maximum curing temperature can be somewhere in the range of 40 to 100 °C. The suggested temperature is in the range of 65 to 80 °C [Powers and Steinour, (1955)]. A maximum curing temperature has been specified by many organizations to ensure the quality of the concrete during its service-life. It reflects the different properties of the cements used by the organization (Table 2.1.).

The above limits specified by the different organizations may not to be practical for some cases in which the concrete is placed in dry conditions. This is because DEF also depends on the later curing conditions. Neck (1988) suggested three different temperature limits for different exposures and curing conditions:

(i) The maximum steam-curing temperature should be 80 °C for interior exposures in dry conditions;

(ii) The maximum curing temperature should be lower than 70 °C for exterior exposure and contact with the earth;

(iii) The maximum curing temperature must not exceed 60 °C for exterior exposure in moist condition.

A prolonged high temperature curing period has found to increase the expansion due to DEF (Ghorab et al. 1980; Lawrence, 1995). Lawrence (1995) examined expansion behaviour of 55 portland cements for a curing temperature range of 65 to 100 °C. He found that a critical curing temperature for DEF is between 65 and 70 °C. Great extension of high temperature curing periods resulted in much reduced expansions. The reason of the stabilization behaviour was not clear.

Table 2.1. Suggested Maximum Curing Temperatures for Concrete

Organization	Limit (°C)	Reference
Iowa State Highway Commission, North America	Curing temperature of 66°C	Meritt and Johnson, (1962)
The European Committee for Standardization	Curing temperature for the heat treatment of precast concrete less than 60 °C for the average temperature and 65 °C for maximum temperature.	European Committee for Standardization (1989)
The German Committee for Reinforced Concrete (1989)	Curing temperature lower than 60 °C for the concrete exposed to damp conditions.	German Committee for Reinforced Concrete (1989)
British Cement Association	Steam-curing temperature should not exceed 70 °C	Lawrence et al (1990)
Canadian standard CAN3-A23.4-M78	Curing temperature for precast concrete less than 70 °C.	Canadian standard CAN3-A23.4-M78

High temperature curing may result in the decreased formation of aluminate, ferrite or sulphoaluminate hydrates in the portland cement paste (Idorn, 1968). Lafuma and Brocard (1950) reported that ettringite decomposes to monosulphate and gypsum at about 60-70 °C. Pure ettringite appears to be more stable than the ettringite in the cement paste (Kalousek and Adams, 1952). The pure ettringite did not decompose in 3 days when placed at temperatures below 100 °C. The ettringite in cement paste completely decomposed forming a solid solution of sulphoaluminates and "phase X" after 16 hours at 50 °C.

§ 2.4.3. Moisture Conditions

Moist exposure is reported to be one of the critical conditions for DEF. The German committee for Reinforced concrete (1989) provided different specifications for precast concretes placed in different moist environments. A lower temperature (60 °C) for heat treatment was required for concrete exposed to damp conditions. Heinz and Ludwig (1987) reported their test results related to the moisture conditions to optimize the conditions for DEF. They found that expansion could be essentially avoided when the concrete was exposed in an environment below 59% R.H. The concrete specimens with similar constituents subjected to similar treatment regimes demonstrated severe

deterioration when they were stored at humidities higher than 60% for four months and then placed in a saturated atmosphere.

§ 2.4.4. Transition Zone

The transition zone at the cement-paste aggregate interface is believed to be the most probable place for ettringite nucleation. Most investigations have shown that ettringite crystals are commonly found in the transition zone in damaged concrete. Hadley (1972) reported in his Ph. D. thesis that ettringite needles were found in the interfacial region after 1-3 days hydration. The reason for ettringite preferentially forming in the transition zone has been explained in different aspects by several workers. Monteiro et al. (1985, 1986, and 1989) indicated that the interface between aggregate and the paste-matrix was a weak zone which possesses higher porosity than the bulk matrix. Calcium hydroxide was orientationally deposited in this region. The thickness of the interface region has been reported to be about 30-50 μm. The most important result of this research was the data indicating that the ettringite content in the transition zone was about 2.5 times that in the paste matrix. The ettringite was mostly formed at 1 μm from the aggregate surface and extended to a 20 μm depth into the paste matrix. Monteiro et al. (1989) examined the transition zone between steel and cement paste. They also found a higher concentration of ettringite crystals in the region near the interface. Calcium hydroxide was deposited with preferred orientation in the transition zone. No evidence was found indicating preferential orientation of ettringite crystals.

§ 2.4.5. The Duggan test

A rapid test (referred to as the Duggan test) to determine the potential expansion due to secondary ettringite formation (SEF) was reported by Grabowski et al (1992). Apparent expansion was found in the concrete samples after several severe heat-drying/re-wetting cycles used to simulate certain service conditions relevant to the performance of railway sleepers. Stark et al. (1992) reported that in addition to the high

temperature curing, concrete structures in connection with drying-temperatures of 60 °C and longer moisture-periods may be damaged. Oberholster et al. (1992) argued that on the basis of their investigation, the Duggan test showed that all tested concrete sleepers were potentially subject to deleterious expansion. However, some of the sleepers did not show any signs of cracking after more than 10 years of service. Idorn and Skalny (1993) doubted that a high expansion potential indicated by the Duggan test (even when the curing temperature of the precast concrete products did not meet the critical condition for DEF) was realistic.

§ 2.5. Case Studies on Deterioration of Concrete Related to DEF

Many case studies have been reported since Kennerly (1965) demonstrated the problems related to the DEF. Deterioration of concrete apparently related to DEF can be divided into three types.

§ 2.5.1. Deterioration Mainly due to DEF

A diagnosis, in some case studies, of the causes of damage concrete has not been conclusive. Neither alkali-aggregate reaction nor external sulphate attack was confirmed. The causes of the problem were mostly attributed to DEF.

Kennerley (1965), the Roxburgh Dam, Otago, New Zealand

Ettringite was found at a cold-joint in the Roxburgh Dam. Kennerley postulated that the reformation of ettringite was due to the different CH concentrations in different areas. Ettringite would decompose at the area where the CH concentration was low in the solution and be transported to areas with high CH concentration. The solubility of ettringite decreases with an increase of CH concentration in the solution.

Jones and Poole (1987), United Kingdom

A large amount of ettringite was found in the cracks around aggregate margins radiating to the paste matrix. The deterioration was examined on the core disks taken from different structures and cured under the same conditions. Only the specimens from

one structure were damaged. This may be due to the previous unknown environmental effect and the cement itself.

Tepponen and Erickson (1987), Finland

Visible deterioration was found in high temperature steam cured (75-80 °C) concrete ties using high early strength cement. The problem was observed after 15 years. The pores and cracks were filled with ettringite.

Heinz, Ludwigs and Rudiger (1987, 1989), Germany

Heat-treated high-strength precast concrete was damaged after several years' exposure to moist environment. The problem mostly appeared in the concrete made with high-early-strength Portland cement and treated at temperatures above 75 °C. The deterioration was believed to be due to the reformation of ettringite at later ages.

Lawrence, Dalziel and Hobbs (1990), United Kingdom

Fifteen prestressed and reinforced concrete structures cast between 1963 and 1969 were examined. Fifteen years later all the concrete made with high early strength cement appeared to have problems with cracking. In addition to some confirmed alkali-silica reaction, ettringite was also found around aggregate grains.

Marusin (1995), East Coast of USA

Deterioration of concrete railway ties related to DEF was reported a few years after their installation. The DEF was believed to originate in the cement paste and the transition zone between the cement matrix and aggregates. Cracking was observed. Ettringite crystallized in the cracks.

§ 2.5.2. Deterioration due to the Combined Factors of Alkali Aggregate Reaction and Delayed Ettringite Formation

It was reported in some case studies that ettringite formation occurred in the presence of alkali-aggregate reaction. It was postulated that the alkali-aggregate reaction enhanced the delayed ettringite formation.

Pettifer and Nixon (1980)

(1) English Midlands (Alkali-aggregate reaction involved) Ettringite was found in pores, voids and at aggregate surfaces in the concrete. No sulphate containing environment was prevalent.

(2) Western England and South Wales (Alkali-aggregate reaction involved) Ettringite was found co-existing with the gel reactant from the alkali aggregate reaction.

Chandra and Berntson (1988), Sweden

Ettringite was found in the concrete along with calcium hydroxide, calcite and gypsum which had been leached to the surface. It was felt that the damage of the concrete was due to a combination of alkali-silica reaction, aggressive reaction of sulphates and alteration of the feldspar aggregate.

§ 2.5.3. Deterioration due to the Combined Factors of Chloride Contamination and Delayed Ettringite Formation

It was reported that chlorides may possibly accelerate delayed ettringite formation, due to formation of monochloroaluminate. This salt can transform to ettringite when sulphate is released from inside the concrete structure.

Pettifer and Nixon (1980), Pirow Street Bridge in Cape Town, South Africa

Ettringite was detected from the concrete made with low alkali cement. The concrete was cracked just 4 years after placing. Chlorides were involved.

Volkwein and Springenschmid (1981)

Ettringite formation was enhanced in a chloride rich environment. Needle-like ettringite crystals was often found in concrete decks near the splashing zone. The sulphate content was essentially as constant. It was felt that the chlorides enhanced the formation of ettringite from the sulphate originating in the cement.

El-Sayed, El-Wahed, and Ali (1987), Egypt

Seven reinforced concrete structures in a marine environment were examined. Deterioration was found in three of them. Ettringite existed in the cracks.

Macleod, Hall and Fallick (1990), Strathclyde, Scotland

Ettringite was detected in the form of white spheres within the air-entrained voids of a concrete bridge. Ettringite deposited along with some unidentified chlorine-rich phase.

Chapter 3

AN INTERNAL SULPHATE SOURCE FOR DELAYED ETTRINGITE FORMATION

- **Formation of Internal Sulphate Source for DEF**
- **Effect of Temperature on Sulphate Adsorption/Desorption by Tricalcium Silicate Hydrates**
- **Effect of Gypsum Addition on Expansion Characteristics - A Further Evidence of DEF Mechanisms**

§ 3.1. Introduction

The potential for deterioration of Portland cement concrete due to secondary ettringite formation has been recognized in the precast concrete industry since Heinz et al. reported cases related to high temperature (>75 °C) steam-cured concrete (Heinz and Ludwig, 1987; Heinz, Ludwig and Rudiger, 1989). They argued that delayed expansion in the concrete was due to the transformation of metastable monosulphate to ettringite when steam curing was followed by normal temperature moist curing at later ages. The chemical composition of the cement, especially the SO_3/Al_2O_3 molar ratio, was considered a critical parameter. It has been recently reported however (Brown and Bothe, 1993) that ettringite is still formed at elevated temperatures (80°C); monosulphate was not observed by XRD. It would appear that another mechanism of supplying sulphate for secondary ettringite formation may exist. Some insight into this apparent controversy is provided by the early research of Lerch et al (1929, 1946). They found that some sulphate added to Portland cement in the form of gypsum could not be accounted for subsequent to hydration. They postulated that the sulphate could be bound into the C-S-H gel structure to form a new phase called "phase X". Kalousek and Adams (1951) believed that "phase X" was a gel containing all oxide constituents of cement. It was transformed from the solid solution of sulphoaluminates in the temperature range 25 to 100 °C. The transformation rate clearly increased with the increase of temperature. Copeland et al. (1967) reported that sulphate combined with C-S-H gel at early ages and was then released at later ages. Odler (1980) also reported similar results from his more recent work in 1980. He found that ettringite apparently formed without any external additions of sulphate indicating that the sulphate for secondary ettringite formation must come from somewhere inside the hydrated Portland cement itself. Taylor (1993) concluded that, although C-S-H gel was not directly involved in reactions leading to ettringite

formation, it did affect the stability of ettringite through its ability to take up both sulphate and aluminate.

The research reported in this chapter focuses on the formation of an internal sulphate source for DEF (section § 3.2). The effect of curing temperature on the sulphate adsorption/desorption characteristics is shown to be an important factor in the development of the internal sulphate source (section § 3.3). DEF is viewed as a sulphate attack problem (referred to as internal sulphate attack). The formation of the internal sulphate source in portland cement products is shown to be a primary source of possible DEF. However, not all the portland cement products undergo deterioration due to DEF. For example, an initial curing temperature > 65 °C is a critical factor characterizing the subsequent behaviour of the products. Additionally sections § 3.2 and 3.3 describe two major experiments designed to demonstrate the mechanisms involved in the formation of the internal sulphate source and its effect on DEF. Section § 3.4 presents further evidence for the mechanisms described in sections § 3.2 and 3.3 through a specially designed experiment.

§ 3.2. Formation of Internal Sulphate Source for DEF

§ 3.2.1. Experimentation

Materials include Type 10 Portland cement (chemical composition (mass %): SiO_2=19.83; CaO=61.21; Fe_2O_3=3.20; Al_2O_3=4.18; MgO=4.09; SO_3=3.93; Na_2O=0.45 and K_2O=0.82.; the Bogue compound composition (mass %) is: C_2S=15.78; C_3S=54.55; C_3A=5.67; C_4AF=9.73) and reagent grade gypsum. Two hundred grams of cement were mixed with 400 ml distilled water in a sealed plastic bottle. The sample was rotated on a roller for 6 months; XRD analysis indicated that the cement paste was well hydrated. The hydrated OPC was filtered and washed with acetone. Then the paste was dried at 65 °C in the oven for 24 hours and was then ground. No carbonate was detected by XRD after the treatment. Two grams of hydrated OPC were weighed and placed into sample bottles.

Gypsum was added into each sample bottle. The amount of gypsum (mass percentage of hydrated OPC) was 5, 10, 15, and 20%. Distilled water (5 ml) was added into each bottle. The sample bottles were rotated on rollers. Four temperatures, 5, 25, 65 and 85 °C, were used in the rehydration treatment of the above mixtures. XRD analysis for initial mineral content was carried out two hours after the sample was fully mixed. The wet sample was used immediately after removal from the sample bottle. Special effort was made to prepare consistently uniform sample coatings to optimize repeatability of results.

§ 3.2.2. Results

The XRD intensities of characteristic peaks for gypsum and ettringite in hydrated Portland cement during rehydration at 5 °C are shown in Figs. 3-1 and 3-2. The d-spacings, 0.756 nm and 0.973 nm were used for following the depletion of gypsum and formation of ettringite. In general, the peak intensities of both gypsum and ettringite for all the samples were very small. Ettringite could be detected in the hydrated Portland cement paste without the addition of extra gypsum. Further ettringite formation after the addition of extra gypsum was not clear.

The XRD peak intensities of gypsum and ettringite in hydrated Portland cement during rehydration at 25 °C are shown in Figs. 3-3 and 3-4. The reduction of the gypsum peak intensity occurred mainly in the first 24 hours for the samples with added gypsum content above 15%. Further ettringite formation after the addition of gypsum was still not readily apparent.

The XRD peak intensities of gypsum and ettringite in hydrated Portland cement during rehydration at 65 °C are shown in Figs. 3-5 and 3-6. The decrease of the gypsum peak intensity with hydration time was much more rapid than those at 5 and 25 °C. The gypsum was mainly consumed in the first day of hydration. Ettringite formation was clearly observed at 65 °C. A large amount of ettringite was formed between one and

three days. The ettringite peak intensity at the first day was only 20% of that of the third day. Minor differences only were detected for the ettringite peak intensity between the samples containing additional gypsum 10, 15 and 20%.

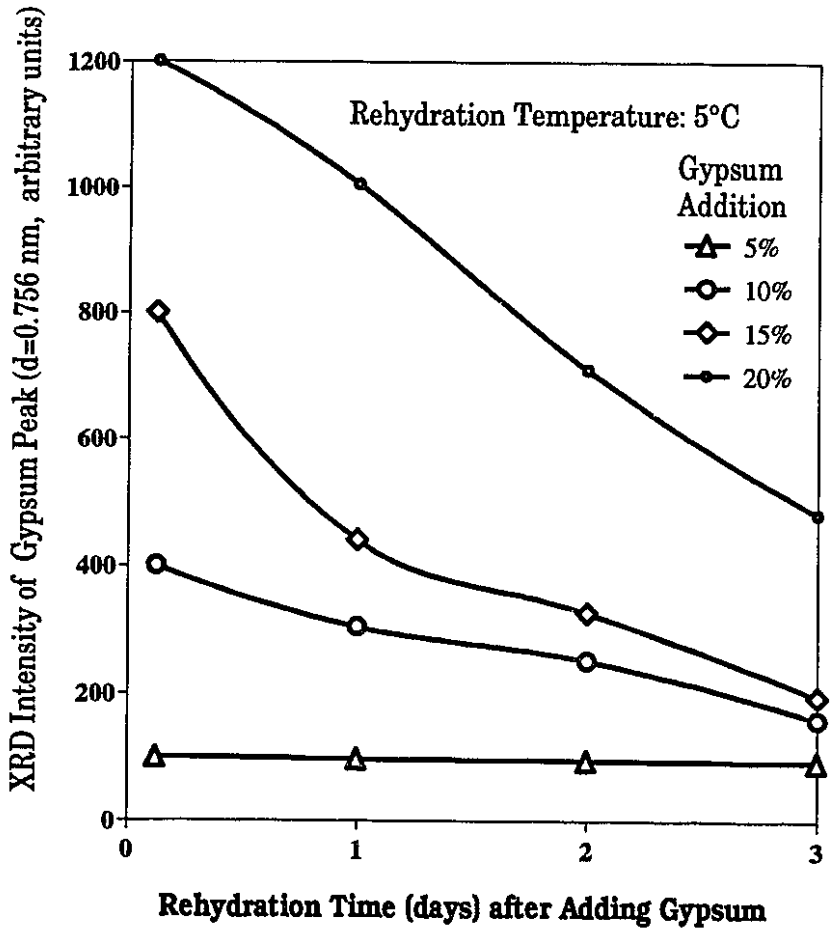


Fig. 3-1. Gypsum consumption in the hydrated Portland cement-gypsum-water system at 5 °C and varying gypsum content.

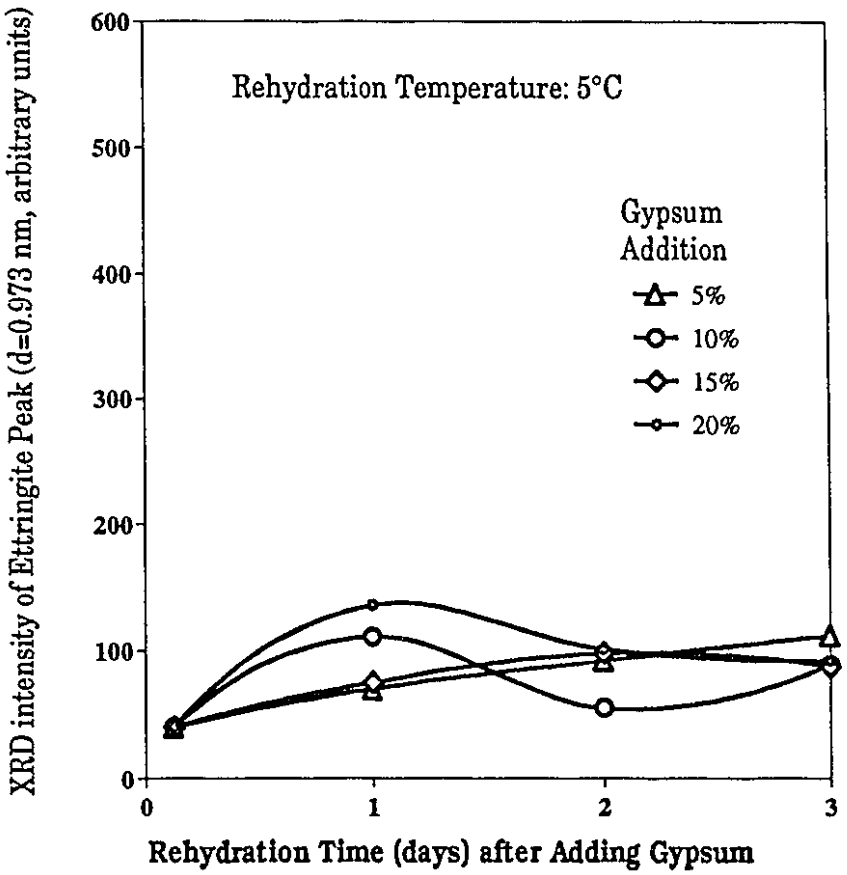


Fig. 3-2. Delayed ettringite formation in the hydrated Portland cement-gypsum-water system at 5 °C and varying gypsum content.

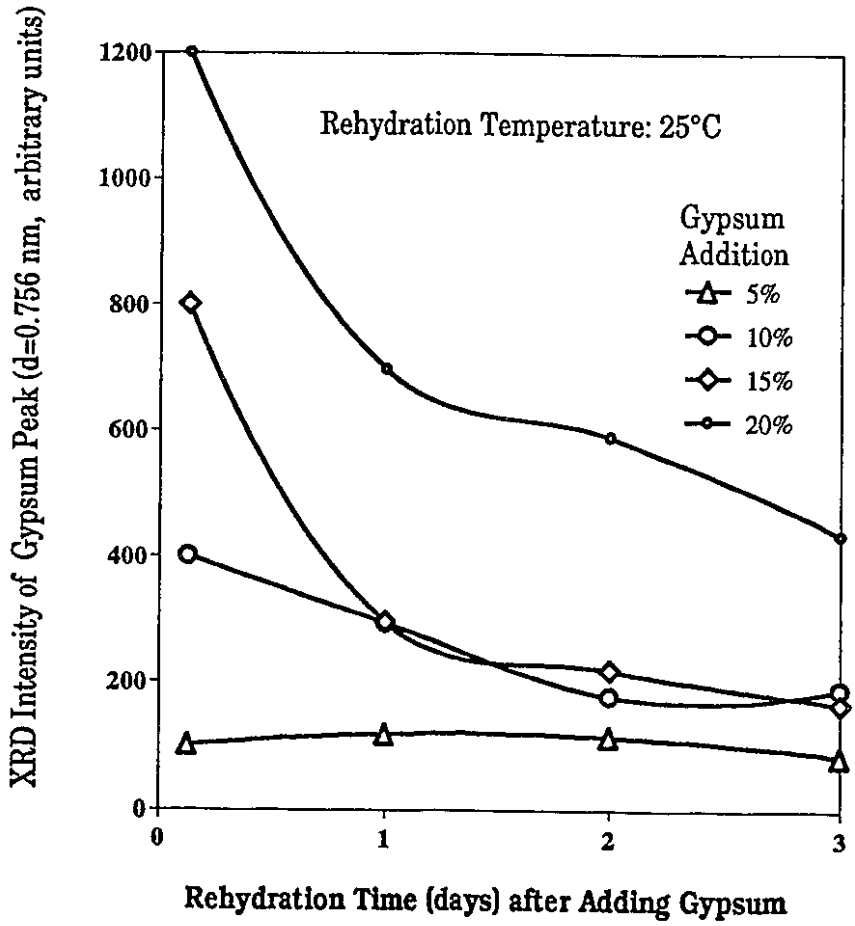


Fig. 3-3.Gypsum consumption in the hydrated Portland cement-gypsum-water system at 25 °C and varying gypsum content.

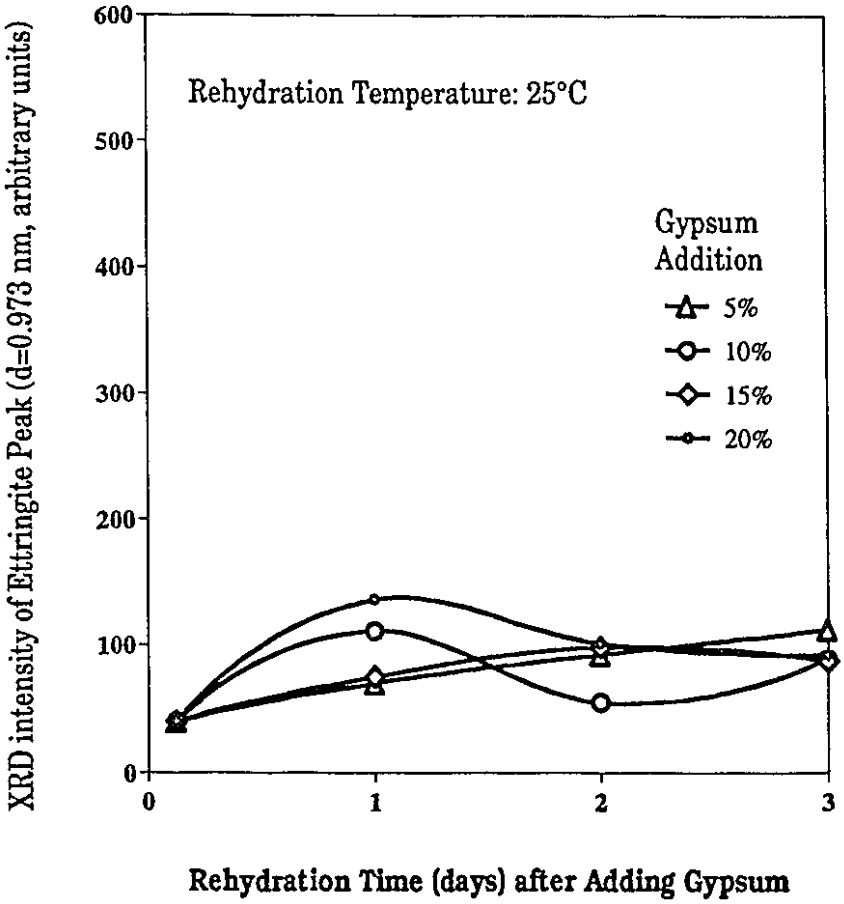


Fig. 3-4. Delayed ettringite formation in the hydrated Portland cement-gypsum-water system at 25 °C and varying gypsum content.

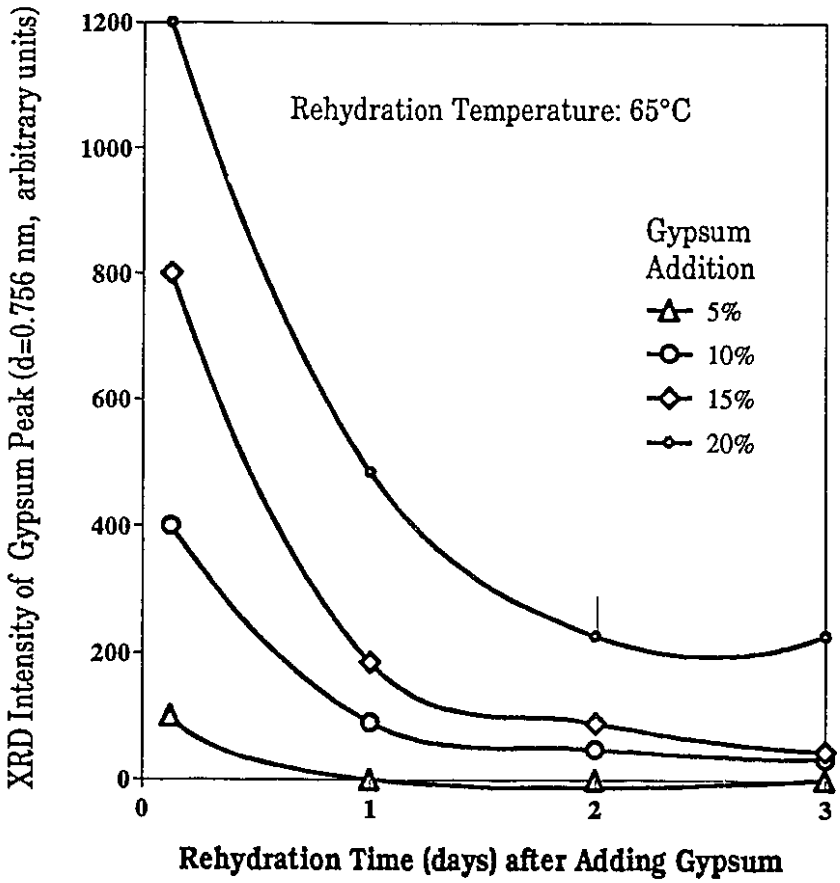


Fig. 3-5. Gypsum consumption in the hydrated Portland cement-gypsum-water system at 65 °C and varying gypsum content.

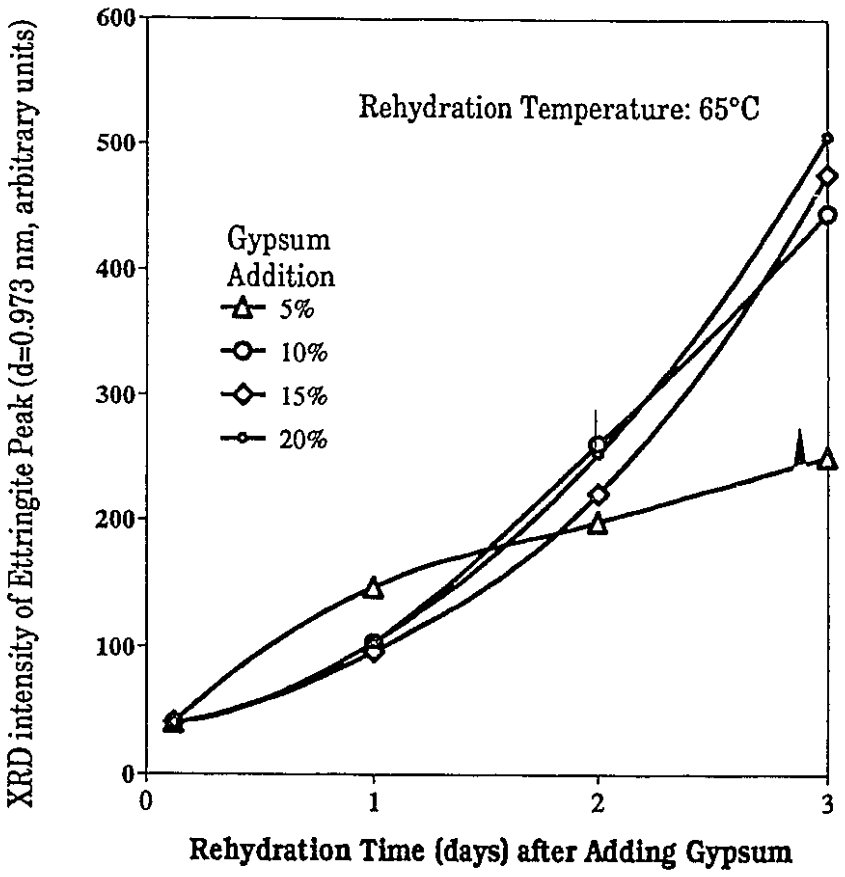


Fig. 3-6. Delayed ettringite formation in the hydrated Portland cement-gypsum-water system at 65 °C and varying gypsum content.

The XRD peak intensities of gypsum and ettringite development in hydrated Portland cement during rehydration at 85 °C are shown in Figs. 3-7 and 3-8. A greater decrease of the gypsum peak intensity in the first day of rehydration was observed at 85°C. Ettringite apparently formed after one day for samples with added gypsum content above 10%. The ettringite peak intensities of the samples containing 10% and 15% additional gypsum were almost similar. The ettringite peak intensities of the samples containing 20% added gypsum were the highest of all at three-days rehydration.

The effect of temperature on gypsum and ettringite XRD peak intensities in hydrated Portland cement paste containing 5% added gypsum is shown in Figs. 3-9 and 3-10. For the samples rehydrated at 65 and 85 °C, the gypsum peak was not detected after one-day. For the samples at 5 and 25 °C, very little change in the gypsum peak was observed after extra gypsum was added. The ettringite formation became obvious when the hydration temperature was higher than 65 °C. The ettringite peak intensity values generally increased with temperature and hydration time.

The effect of temperature on gypsum and ettringite XRD peak intensities in hydrated Portland cement paste containing 10% added gypsum is shown in Figs. 3-11 and 3-12. The gypsum content reduced slowly and only a small amount of ettringite formed at 5 and 25 °C. The gypsum peak intensities decreased rapidly at one day for samples rehydrated at 65 and 85 °C. Ettringite formation occurred mainly after one day.

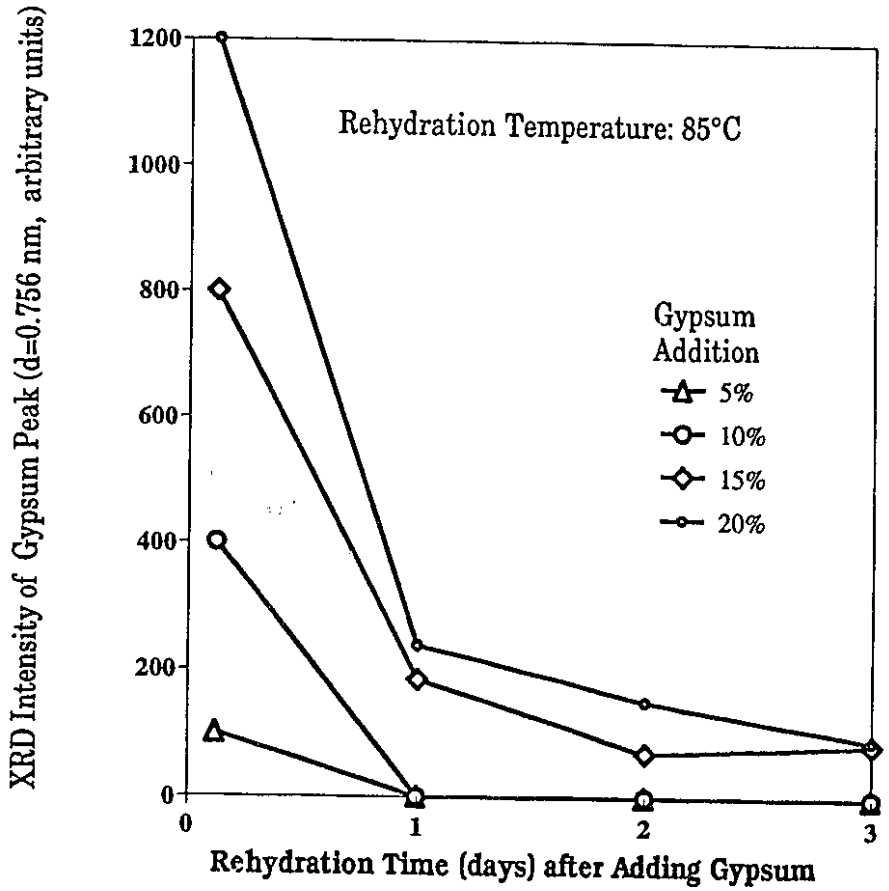


Fig. 3-7. Gypsum consumption in the hydrated Portland cement-gypsum-water system at 85 °C and varying gypsum content.

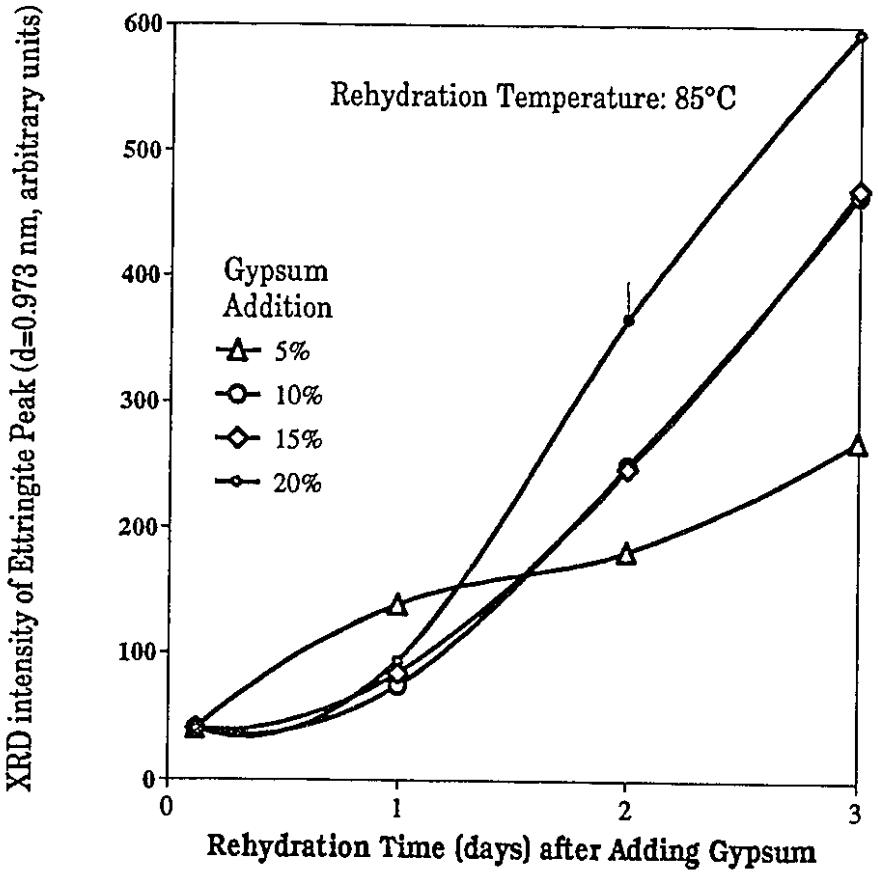


Fig. 3-8. Delayed ettringite formation in the hydrated Portland cement-gypsum-water system at 85 °C and varying gypsum content.

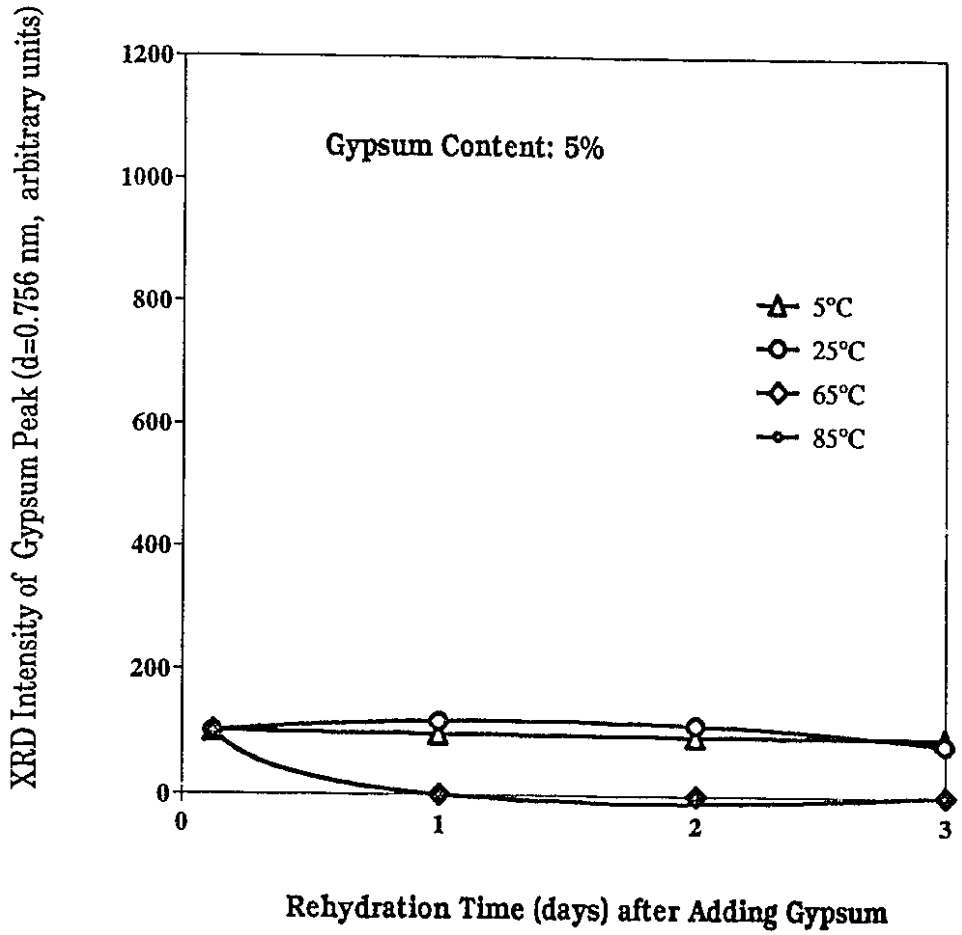


Fig. 3-9. Effect of temperature on gypsum consumption in the hydrated Portland cement-gypsum-water system containing 5% added gypsum.

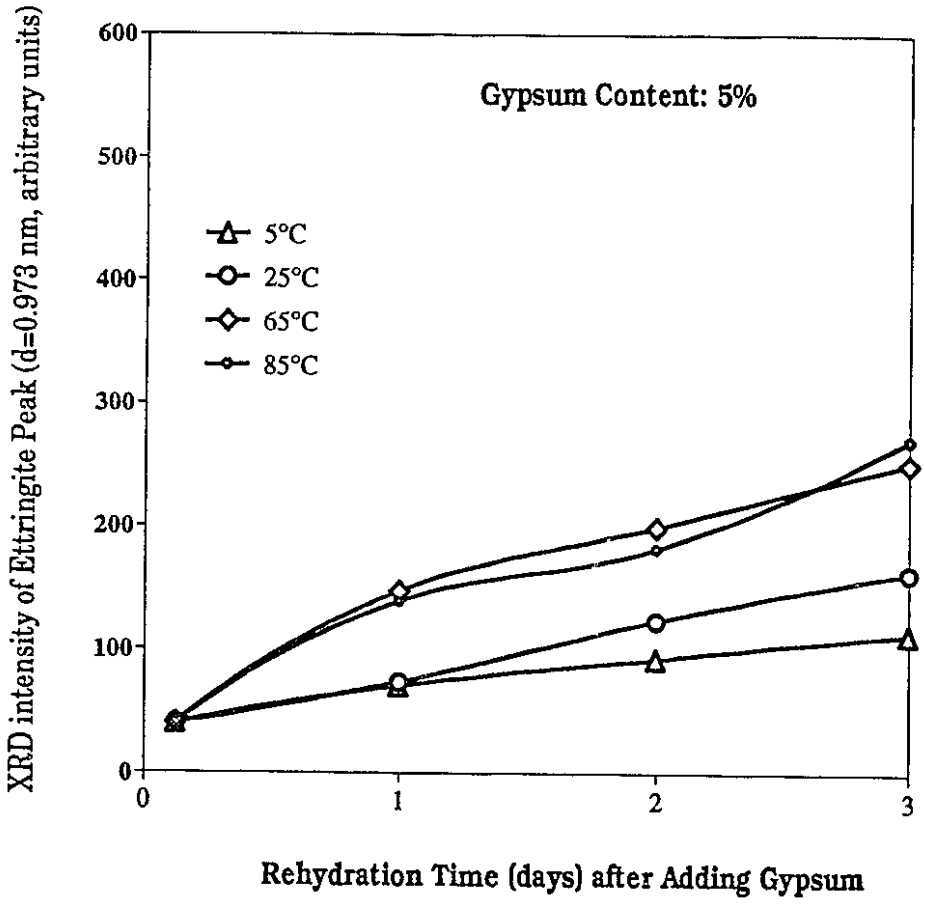


Fig. 3-10. Effect of temperature on delayed ettringite formation in the hydrated Portland cement-gypsum-water system containing 5% added gypsum.

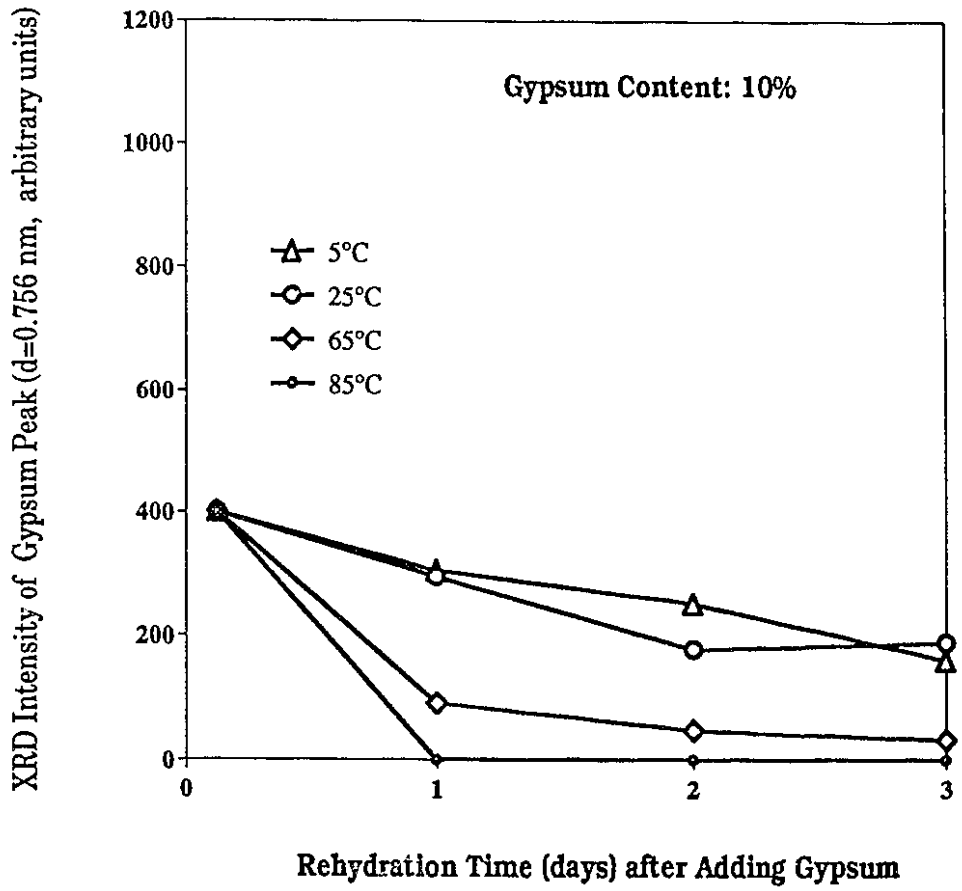


Fig. 3-11. Effect of temperature on gypsum consumption in the hydrated Portland cement-gypsum-water system containing 10% added gypsum.

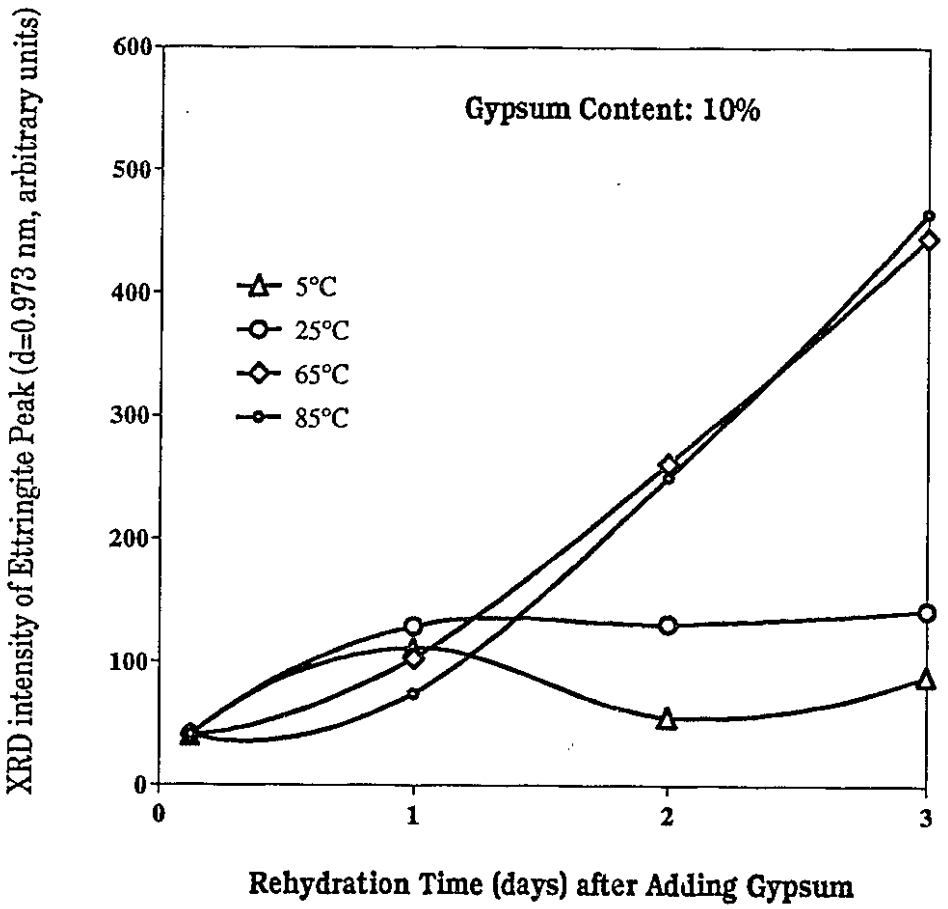


Fig. 3-12. Effect of temperature on delayed ettringite formation in the hydrated Portland cement-gypsum-water system containing 10% added gypsum.

Temperature played an important role in the reduction of the gypsum peak intensity for the samples containing 15% added gypsum (Fig. 3-13). The gypsum peak intensity decreased more rapidly with the increase of rehydration temperature from 5 to 85 °C. The consumption of gypsum mainly occurred in the first day of rehydration at 65 and 85 °C. Ettringite formation was accelerated after one-day (Fig. 3-14). Ettringite formed very slowly in samples cured at 5 and 25 °C. The amounts were similar. The amount of ettringite formation was also similar at 65 and 85 °C. A critical change in the amount of ettringite formation occurred between 25 and 65 °C.

The amount of ettringite formation for the samples containing 20% added gypsum (Fig. 3-15) was similar to those described in Fig. 3-13. The effect of temperature on gypsum reduction was more pronounced. The gypsum peak intensity greatly decreased during the first day of hydration. The gypsum peak intensity reduced from 1000 units to 200 units as the temperature increased from 5 ° to 85 °C. Little difference in ettringite peak intensity was found after one-day hydration at 5 and 25 °C. However, ettringite formation was clearly accelerated after one-day as the temperature increased to above 65 °C (Fig. 3-16).

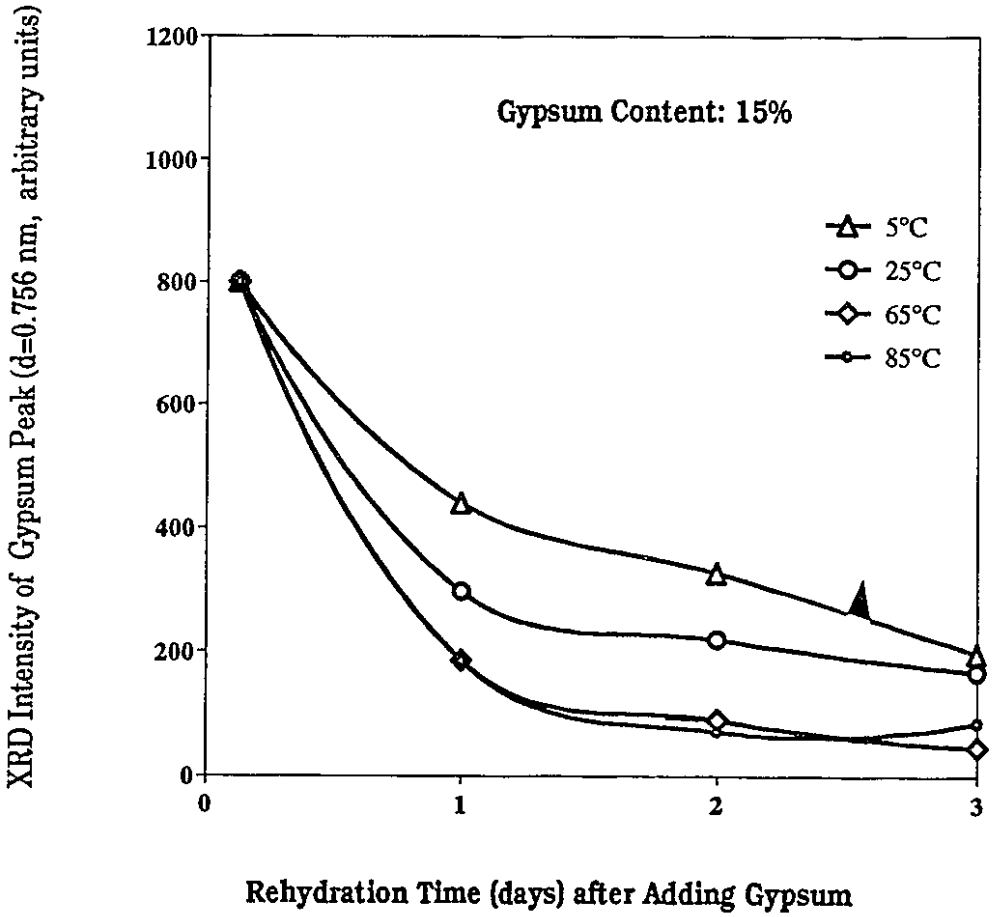


Fig. 3-13. Effect of temperature on gypsum consumption in the hydrated Portland cement-gypsum-water system containing 15% added gypsum.

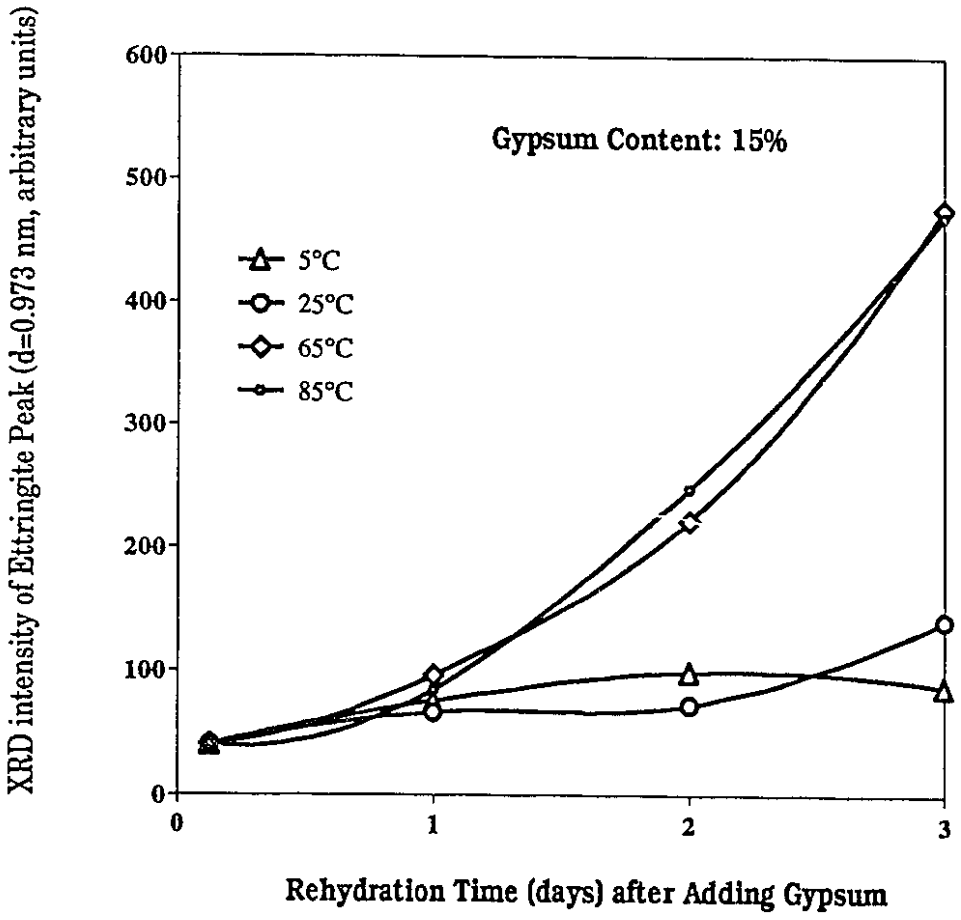


Fig. 3-14. Effect of temperature on delayed ettringite formation in the hydrated Portland cement-gypsum-water system containing 15% added gypsum.

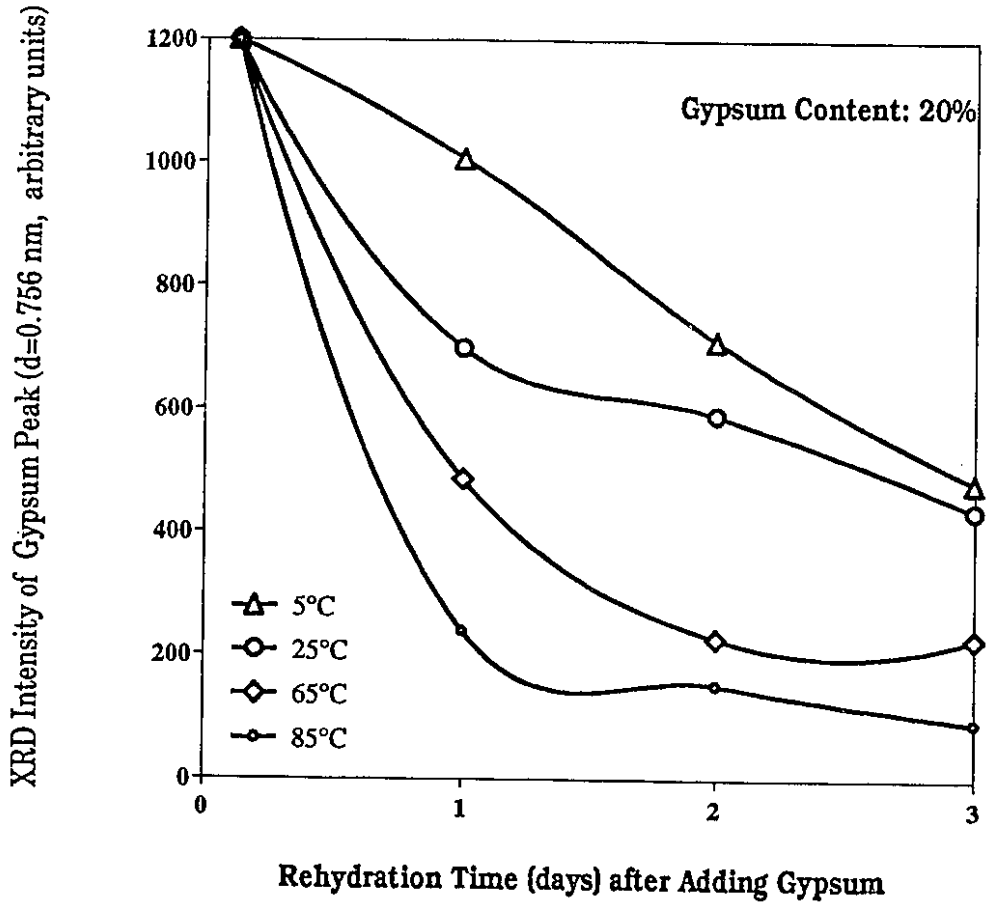


Fig. 3-15. Effect of temperature on gypsum consumption in the hydrated Portland cement-gypsum-water system containing 20% added gypsum.

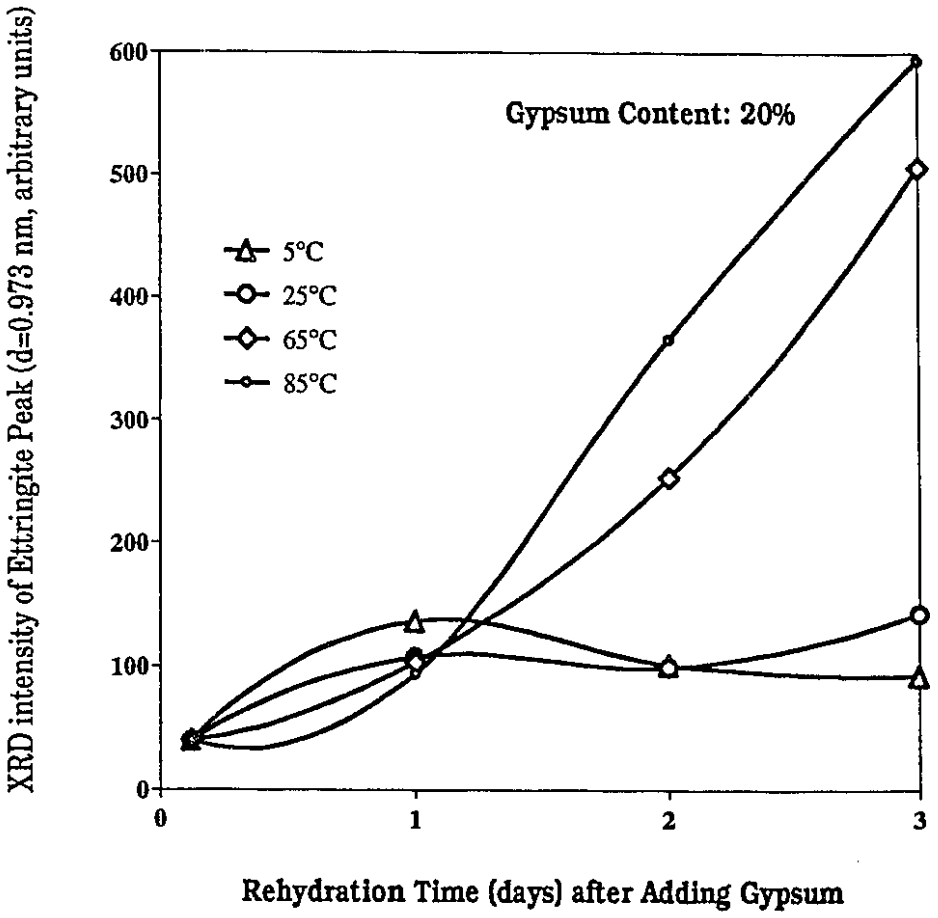


Fig. 3-16. Effect of temperature on delayed ettringite formation in the hydrated Portland cement-gypsum-water system containing 20% added gypsum.

§ 3.2.3. Discussion

Based upon semi-quantitative XRD analysis, It can be inferred from this study that there is a correspondence between gypsum depletion and ettringite formation in the hydrated cement - gypsum - water system particularly at high temperatures (65-85 °C). Gypsum is mainly consumed in the first day after which ettringite formation accelerates. Two competitive reactions appear to influence the rate of gypsum consumption and ettringite formation. Assessment of the kinetics of these reactions should provide some insight as to the mechanisms controlling delayed ettringite formation in high temperature steam-cured Portland cement paste.

§ 3.2.3.1. Gypsum depletion

Mechanisms of gypsum depletion detected by XRD analysis of the hydrated cement - gypsum - water system are considered as follows:

(1) Dissolution in hydrated Portland cement paste solution

The solubility of gypsum is in range of 0.0022 to 0.0027 gram/ml water at 5-90 °C. Supersaturation of gypsum in the Portland cement paste system can occur after a few minutes of hydration (Taylor, 1990). In this study gypsum was added to hydrated Portland cement paste prepared with a water/cement ratio of 2.5. The gypsum/water ratios are correspondingly 0.02 - 0.08 gram/ml. The gypsum content in the water is so high that only a small amount of the gypsum (less than 10%) will dissolve in the water even at 85 °C. The solubility of gypsum will be less than in pure water as hydrated Portland cement paste is rich in calcium hydroxide. Therefore dissolution of gypsum in the paste is negligible and cannot account for the gypsum depletion.

(2) Reaction to form ettringite

Test results indicate that only a limited amount of ettringite is formed during the period of major gypsum consumption.

(3) Consumption by C-S-H gel

Odler reported that, 100 g of C_3S can incorporate 9.8 g SO_3 (Odler, 1980). Similar results were also obtained by Copeland et al (1967), Bentur (1976) and Mehta and co-workers (1979). Theoretically two grams of hydrated Portland cement (containing about 1.1 gram C_3S) can combine with about 0.25 gram gypsum (12%). Test results reported here are in very close agreement. It would appear then that the sulphate adsorption by C-S-H gel is a strong possibility. The surface chemistry of C-S-H gel has been extensively studied. It can be hypothesized that the large surface area of C-S-H gel makes it possible to adsorb sulphate ions. This adsorption reduces the sulphate ion concentration in cement paste. Gypsum then dissolves until C-S-H is saturated with sulphate. The adsorption process can occur very rapidly at early ages and then slow down. The adsorption rate is strongly enhanced by increasing temperature.

§ 3.2.3.2. Competitive reactions involving gypsum, hydrated calcium aluminates and C-S-H gel

Ettringite formation in the hydrated cement - gypsum - water system is clearly delayed in contrast to the rapid depletion of gypsum. It generally occurs after 24 hours at 65 to 85 °C when most of the gypsum has been consumed. Two competitive reactions involving sulphate consumption are postulated:

(1) Sulphate consumption by C-S-H gel

$$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O \qquad (3.1)$$

$$nSO_4^{2-} + m\ \text{C-S-H} \rightleftharpoons \text{Phase X} \qquad (3.2)$$

where "phase X" is a phase containing C-S-H and sulphate as defined by Lerch [4,5]

(2) Sulphate -aluminate reaction to form ettringite

$$C_4AH_{13} + 3\ SO_4^{2-} + 2CH + 17H \rightleftharpoons C_3A \cdot 3C\bar{S} \cdot H_{32} \qquad (3.3)$$

It appears that on the basis of test results the first reaction is faster than the second one, and greatly accelerated by increasing temperature at very early ages. In this stage,

C-S-H gel consumes sulphate to form "phase X" at high temperature (above 65 °C), and ettringite formation is limited. The first reaction reaches dynamic equilibrium after one day and the sulphate concentration in C-S-H gel approaches saturation; the formation of ettringite then becomes controlling. Sulphate can be continuously supplied by release from "phase X" during the process of ettringite formation. The rate of ettringite formation is probably controlled by the diffusion rate of sulphate from C-S-H gel. This process and the inherent dynamic equilibrium is maintained until the sulphate is completely released and reacted. The reaction process may last for long periods depending on the diffusion rate and microstructural characteristics of the hardened Portland cement paste.

§ 3.2.3.3. Delayed ettringite formation

Grusczscinski et al (1993) reported that ettringite formation from aluminates (C_3A and HAC) and gypsum generally occurred within 40 minutes at 50 to 70 °C. Ettringite formation is clearly delayed for about 24 hours in the system studied. Two reasons are suggested:

(1) Ettringite formation rate from hydrated calcium aluminates is apparently lower than from anhydrous calcium aluminates (1993).

(2) Sulphate adsorption by C-S-H gel reduces the degree of supersaturation and reduces the rate of ettringite formation. The release of sulphate ions from C-S-H gel is diffusionally controlled. In hardened cement paste, the release rate of sulphate should be much slower than presented in this study. A large amount of ettringite is produced in the sample with 20% gypsum (Fig. 3-4) during three days rehydration at 85 °C indicating that there is an appreciable amount of calcium aluminate phase available in hydrated Portland cement. These aluminates are a source for ettringite formation at later ages. Delayed ettringite formation can result from release of sulphate from the C-S-H gel.

§ 3.2.3.4. Potential for delayed ettringite formation in high temperature steam-cured Portland cement paste

Elevated temperature enhances the rate of gypsum consumption. It does not however appear to affect the manner of ettringite formation during the first day of hydration. No monosulphate was detected by XRD even at 85 °C hydration. This has also been confirmed by Brown (1993) and Grusczscinski (1993). In high temperature steam-cured Portland cement paste, the hydration rate of C_3S is greatly increased. More C-S-H gel forms and correspondingly more sulphate is consumed by the C-S-H phase. This consumption reduces sulphate concentration in the paste and limits ettringite formation. The hydrated calcium aluminates remaining in the cement paste matrix react further with the sulphate released from the C-S-H gel at later ages. The rate of delayed ettringite formation may depend on the diffusion rate of sulphate from hardened C-S-H gel. Any measure to reduce the sulphate consumption by C-S-H gel should be helpful to prevent deterioration from delayed ettringite formation.

§ 3.2.4. Conclusions

It appears that two competitive reactions in terms of gypsum consumption exist between C-S-H gel and hydrated calcium aluminates in the hydrated cement - gypsum - water system. The increase of temperature apparently accelerates sulphate adsorption by C-S-H gel. Ettringite formation is relatively temperature independent in the range 65 to 85 °C during the first day of hydration. This would appear to account for delayed ettringite formation in high temperature steam-cured Portland cement based materials.

§ 3.3. Effect of temperature on sulphate adsorption/desorption by tricalcium silicate hydrates

§ 3.3.1. Experimentation

The materials used in this study include triclinic tricalcium silicate (C_3S), tricalcium aluminate (C_3A) (supplied by CTL, Skokie IL.) and reagent grade gypsum.

The C_3S was hydrated in excess water until the presence of the anhydrous C_3S mineral could not be detected by XRD analysis. The hydrated C_3S was ground in acetone to similar fineness as Portland cement (amount passing 75-μm sieve was equal to 97.87%, ASTM C 184-90). It was dried at 65°C for 24 hours. Two grams of hydrated C_3S were placed in labelled sample bottles. Gypsum was added into the sample bottles. The gypsum content was 1, 3 and 5% by mass of C_3S. Two ml of distilled water were added and the samples were mixed by rotating on rollers for 30 minutes. XRD analysis was performed after the sample was uniformly mixed. A wet sample was used for the XRD test. The paste sample was carefully coated on a glass slide. Sample coatings were made using an identical procedure to ensure consistency. Samples were moist cured at 25, 65 and 85 °C for three days after the first XRD test. XRD analysis was continued at designated times during the curing process until gypsum was no longer detected. In subsequent experiments, C_3A in the amount of 5% by mass of hydrated C_3S was added into the same samples after the curing period and XRD analysis was carried out every 24 hours.

§ 3.3.2. Results and discussion

Concrete damage due to delayed ettringite formation usually appears after six months hydration; gypsum, however, has generally disappeared in cement paste before 28 days. The sulphate source in hydrated Portland cement paste has been identified in the research mentioned above. A sulphate source from C-S-H gel should exist for all Portland cement - based materials. Deterioration, however, has only been reported for concrete cured at high temperature. A temperature increase during the curing period is critical for delayed ettringite formation. The effect of temperature on sulphate adsorption by C_3S hydrates is shown in Fig. 3-17. The initial XRD intensity of gypsum at d-space=0.79 nm for the samples containing 5% gypsum was about 160 units. The reduction of gypsum with hydration time was apparently accelerated by the increase of

temperature. The gypsum peak intensity for the sample cured at 85 °C dropped linearly to zero after only 3-5 hours hydration. Gypsum adsorption was clearly delayed for about 1.5 hour and then the gypsum peak intensity decreased to zero in another 6 hours at 65 °C. No evidence of gypsum depletion was found in the first 24 hours at 25 °C. A sudden drop in gypsum peak intensity occurred at 27 hours hydration and gypsum disappeared at 30 hours hydration.

Odler (1980) concluded that sulphate is physically adsorbed to the large surface of the C-S-H gel and can be readily desorbed under certain conditions. In his work, more than 95% sulphate could be extracted from C-S-H gel by saturated calcium hydroxide solution. In the present studies, C_3A was used as an extractant to demonstrate the desorption characteristics of C-S-H gel which had adsorbed sulphate at different temperatures. The hydration of C_3A was found to be retarded in different degrees. The XRD intensity of the C_4AH_{13} peak at d-space=0.79 nm as a function of rehydration time after adding C_3A is shown in Figs. 3-18, 3-20 and 3-22. It is apparent that C_4AH_{13} formation was strongly suppressed with an increase of gypsum content in C-S-H gel. No C_4AH_{13} formed during the first day of rehydration in samples containing 5% gypsum while a value of about 3000 units for the C_4AH_{13} peak intensity was obtained for samples containing only 1% gypsum. Delayed C_4AH_{13} formation was believed to be attributed to retardation by sulphate. A large difference in C_4AH_{13} formation was found between the samples containing 1 and 3% gypsum; a gypsum content between 3 and 5% had a minimal effect at 3-days rehydration. Ettringite was detected in samples containing 3 and 5% gypsum (Figs. 3-19, 3-21 and 3-23.). The ettringite formation appeared to be nearly independent of both gypsum content at this level and sulphate adsorption temperature. It is postulated that ettringite formation is controlled by both the aluminate dissolution rate from C_3A surfaces and the sulphate desorption rate from C-S-H gel. Sulphate adsorption rate decreases with an increase of sulphate adsorbed by C-S-H gel. Correspondingly the

sulphate desorption rate increases with an increase of sulphate content in C-S-H gel. The sample containing 5% gypsum should release sulphate faster than that containing 3% gypsum and correspondingly lower C_4AH_{13} formation resulted due to the well known sulphate retardation effect. No ettringite was detected in the samples containing 1% gypsum indicating that not all adsorbed sulphate may desorb from C-S-H gel. Limited sulphate may remain in the C-S-H structure under normal environmental conditions.

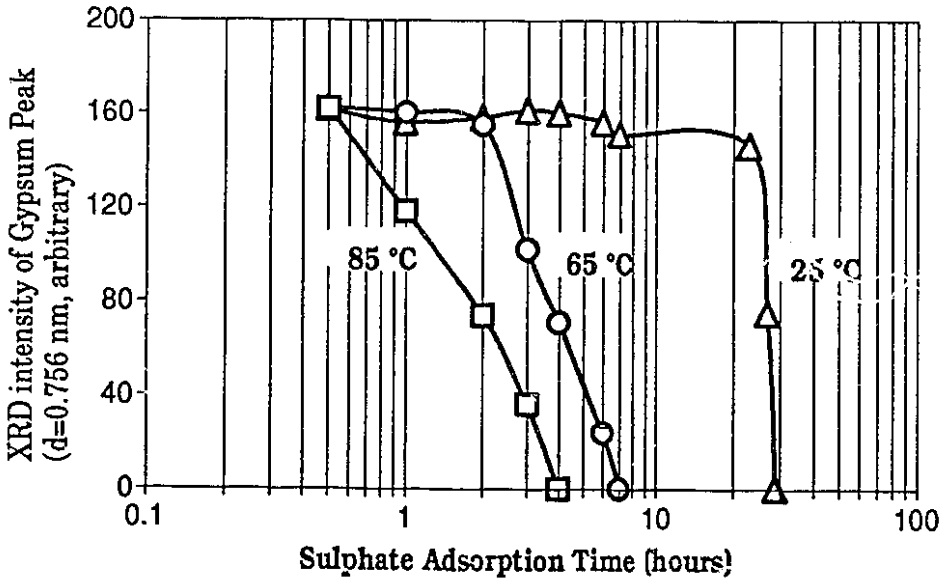


Fig. 3-17. Effect of temperature on sulphate adsorption by C_3S hydrates (Gypsum addition = 5%)

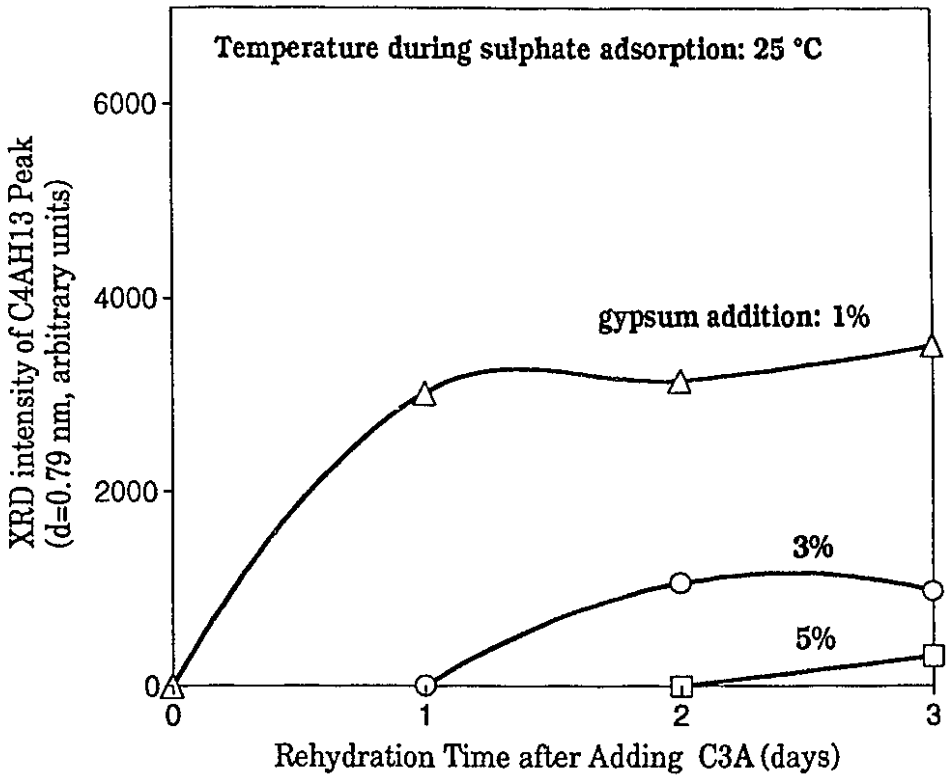


Fig. 3-18. Formation of C_4AH_{13} in the C-S-H - Gypsum - C_3A - CH -H_2O system.

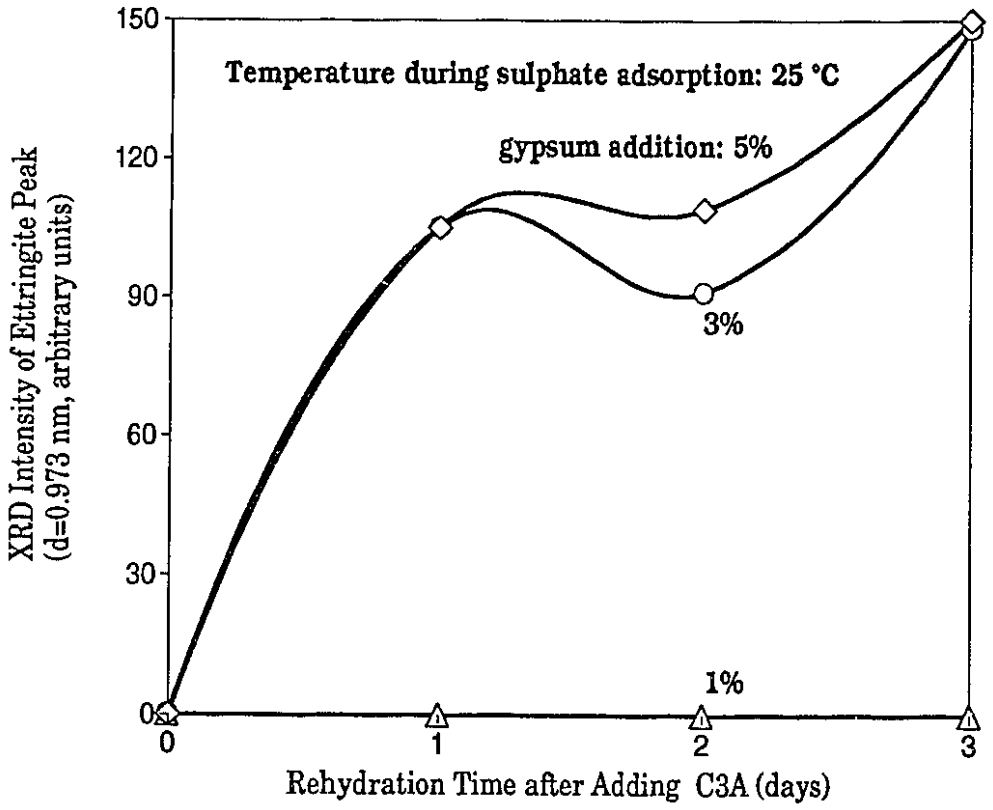


Fig. 3-19. Formation of ettringite in the C-S-H - Gypsum - C_3A - CH -H_2O system.

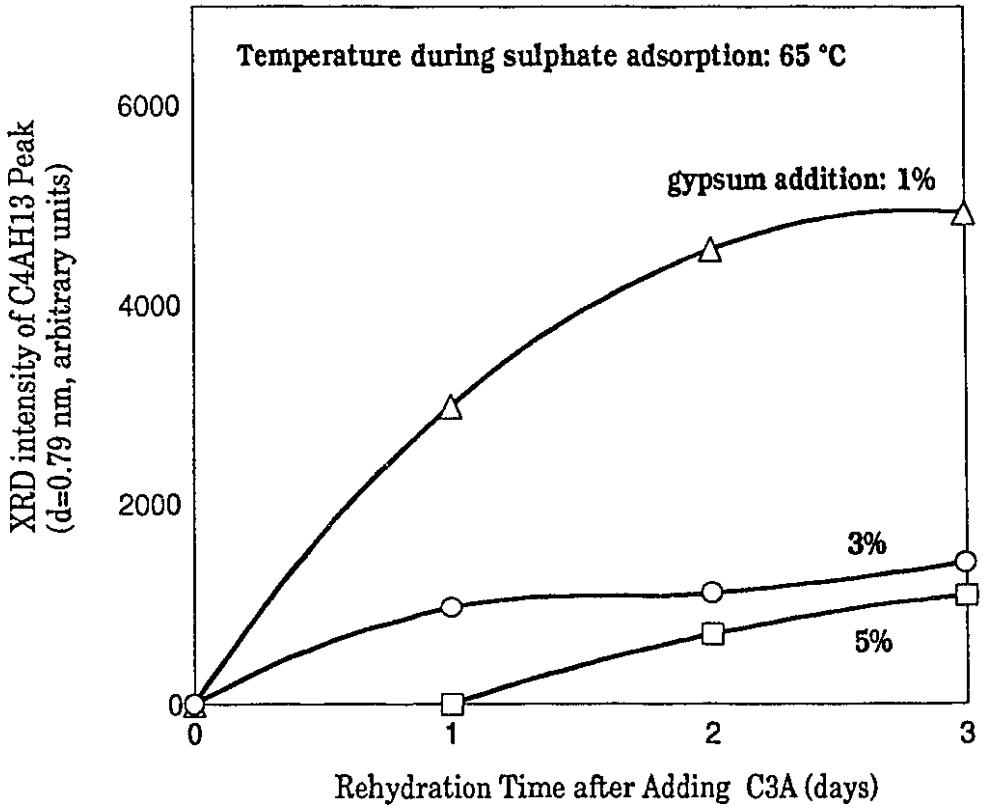


Fig. 3-20. Formation of C_4AH_{13} in the C-S-H - Gypsum - C_3A - CH -H_2O system.

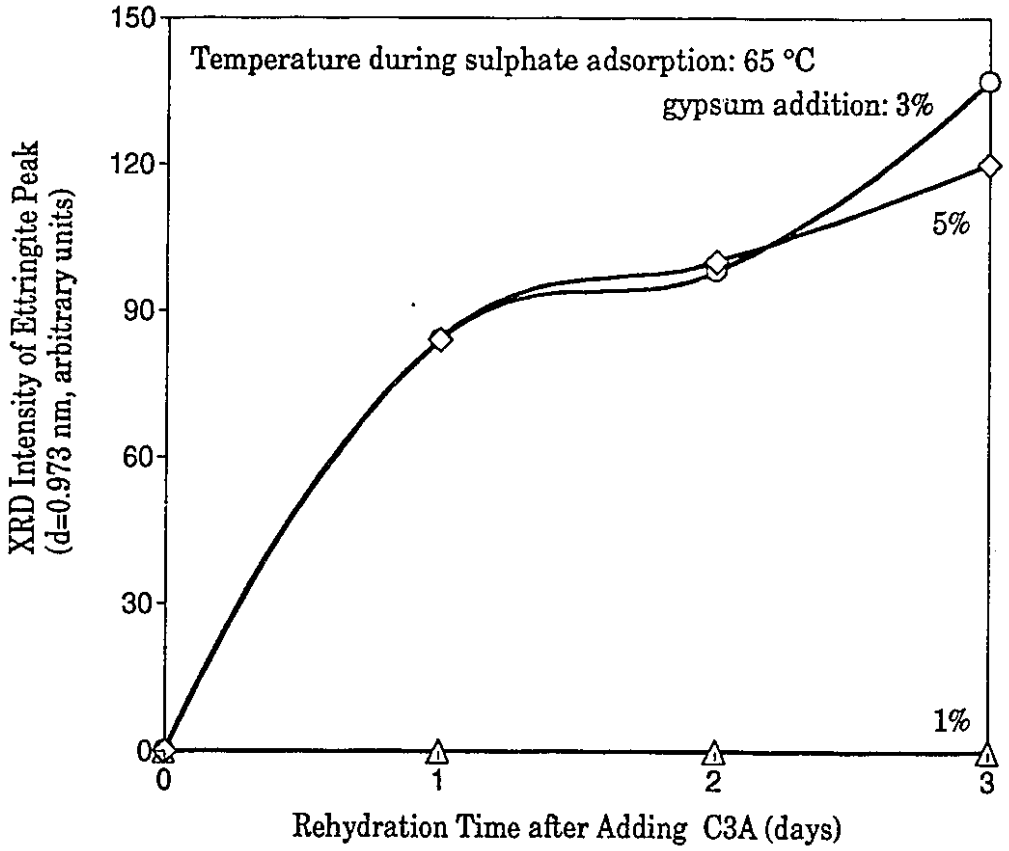


Fig. 3-21. Formation of ettringite in the C-S-H - Gypsum - C_3A - CH -H_2O system.

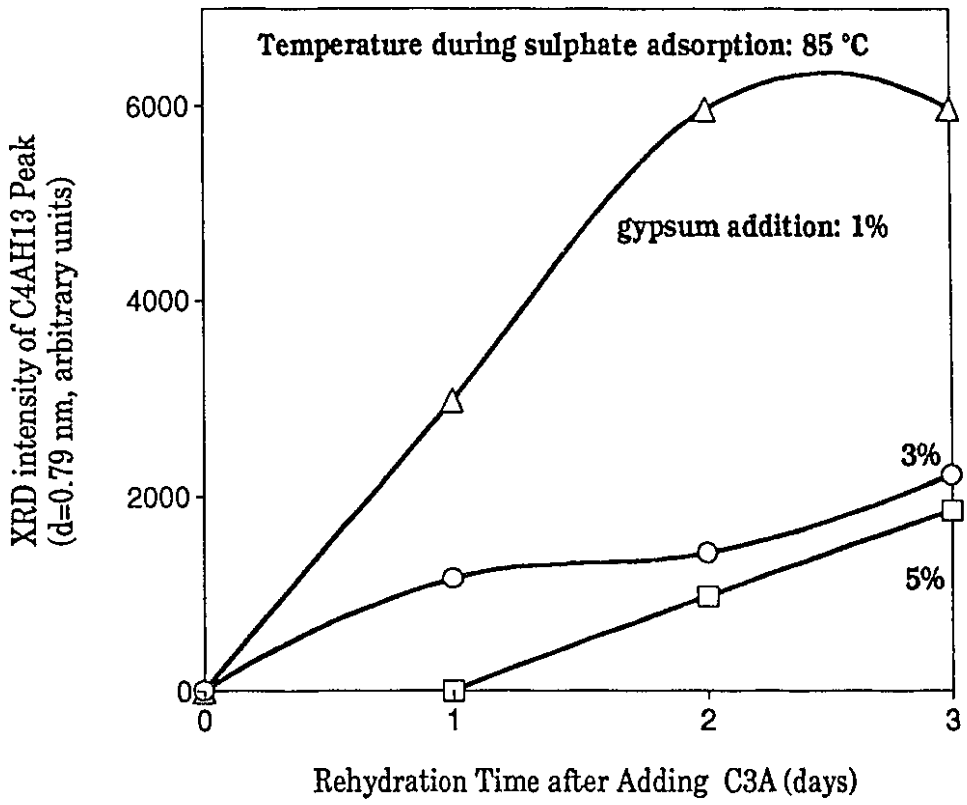


Fig. 3-22. Formation of C_4AH_{13} in the C-S-H - Gypsum - C_3A - CH -H_2O system.

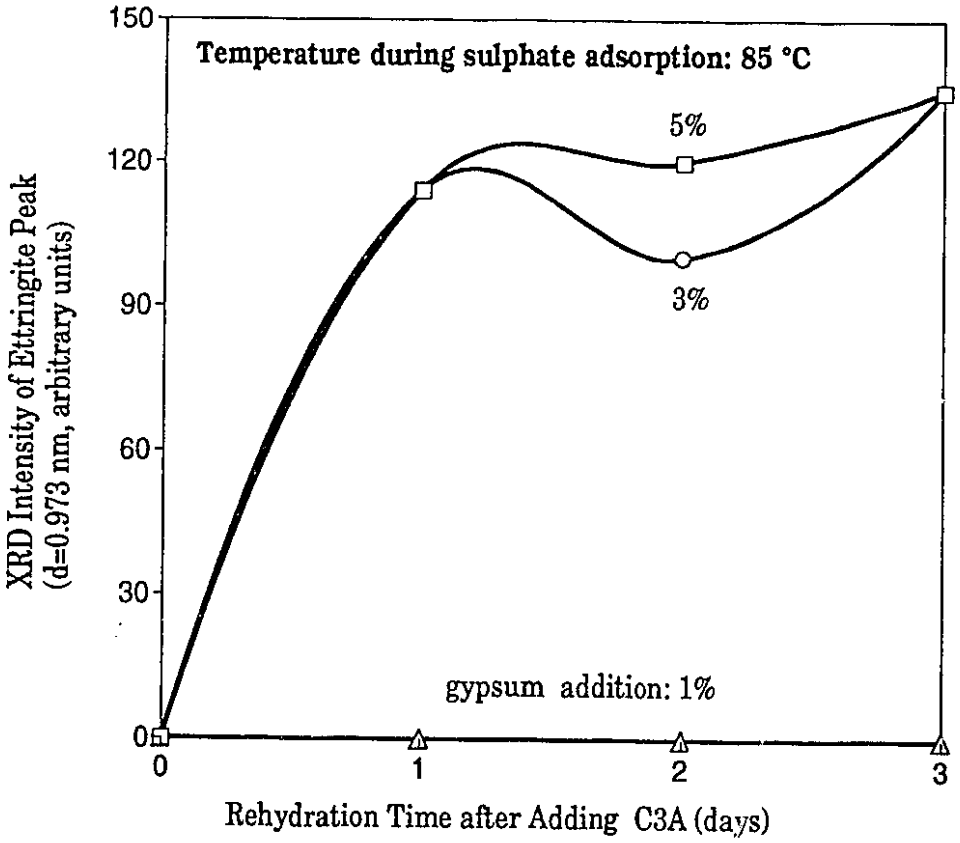


Fig. 3-23. Formation of ettringite in the C-S-H - Gypsum - C_3A - CH -H_2O system.

The temperature at which sulphate was adsorbed by C-S-H gel also affected the C_4AH_{13} formation during rehydration (from Fig. 3-18 to 3-23.). Less retardation effect on C_4AH_{13} formation was found when the temperature was increased during the adsorption of sulphate by C-S-H gel. If the retardation mechanism is assumed to be the same as discussed above, the difference in the C_4AH_{13} formation rate is also attributed to the free sulphate concentration in the rehydration system. It can be deduced that the sulphate adsorbed at higher temperature by C-S-H gel will be desorbed more slowly than that adsorbed at lower temperatures when C_3A as an extractant exists. The lower concentration of sulphate results in a smaller retardation effect on the sample treated at high temperature during sulphate adsorption. Ettringite formation is apparently less susceptible to temperature change. It is postulated that ettringite formation rate is controlled by the sulphate desorption rate and the total reaction surface of both C_3A and its hydrates. The C_3A / C_4AH_{13} ratio apparently decreases with hydration, but the change of total reaction surface area available for formation of ettringite is relatively less.

It is suggested, based upon the study on pure C-S-H - gypsum - C_3A -water system, that there are significant differences between Portland cement paste treated by high temperature curing and paste cured at normal temperature that relate to the supply of internal sulphate and delayed ettringite formation:

(1) The silicate hydrates of Portland cement adsorb sulphate more efficiently during high temperature curing. This sulphate adsorption reduces the sulphate concentrations in the cement paste solution, limits ettringite formation for a certain period, and correspondingly increases the availability of Al-bearing material for delayed ettringite formation.

(2) The silicate hydrates containing sulphate adsorbed at high temperature as opposed to low temperature desorb sulphate more slowly. The slower release of sulphate from C-S-H gel results in a favorable environment for ettringite formation at later ages.

The release may last for a very long period depending on the diffusion rate of sulphate in hardened cement paste and its microstructure.

§ 3.3.3. Conclusions

The C-S-H gel will adsorb sulphate faster at high temperature resulting in a relatively quick disappearance of the gypsum phase in C-S-H - gypsum mixtures. The C-S-H gel, containing sulphate adsorbed at high temperature, will desorb the sulphate more slowly than gel that has adsorbed sulphate at normal temperature. A slower release of sulphate from an internal sulphate source may be critical for delayed ettringite formation in high temperature cured Portland cement paste.

§ 3.4. Effect of Gypsum Addition on Expansion Characteristics of a DEF-suspect Cement Mortar - A Further Evidence of DEF Mechanisms

§ 3.4.1. Experimentation

Cement mortars made with Type 30 portland cement (chemical composition (mass %): SiO_2=19.87; CaO=62.34; Fe_2O_3=1.91; Al_2O_3=5.09; MgO=2.98; SO_3=4.08; Na_2O + K_2O=0.60.; the Bogue compound composition (mass %) is: C_2S=16.07; C_3S=54.21; C_3A=10.26; C_4AF=5.81; Blaine fineness 5682 cm^2/g), reagent gypsum ($CaSO_4 \cdot 2H_2O$) and river sand were used in this research. The water/(cement+gypsum) ratio was 0.48. The sand/cement ratio was 2.75. The additions of gypsum in the portland cement were 0, 5, 10, 12.5, 15, 20, 25 and 30% by mass of the cement.

The mortars were mixed with the procedure described in ASTM Method C 305. Two 1x1x6-in.test specimens for each cement were prepared. The temperature of the molding room, dry materials, and mixing water was maintained at 23 °C and the relative humidity of the molding room was about 50%.

The specimens were then placed in the moist room. All test specimens in the molds were kept in the moist room with upper surfaces exposed to the moist air but protected from dripping water. One set of the specimens was moist cured at 23 °C before

demolding. The other set of companion specimens was prepared for curing at high temperature. These specimens were put in a plastic container after a pre-storage of about 1 hour. The container with the test specimens was tightly covered and sealed. The container was placed in an oven. The temperature in the container was raised to 90°C in 60 min and maintained for 12 hours. The heat unit was turned off at 12 hours and the test specimens were cooled for 4 hours by opening the oven door. The specimens were removed from the molds, properly identified, and placed in water maintained at 23°C for 6 hours prior to making initial length measurements. The relative humidity in the container was maintained at 100%. The specimens were subsequently dried in an oven maintained at 85°C for 24 hours, and then cooled to room temperature after the initial length measurement. All the specimens (both 23°C and high temperature cured) were then stored in saturated lime water in a tank in the moist room at 23°C.

The specimens were removed from water storage, and wiped with a damp cloth before further measurements were taken. The lengths of the specimens were measured using an electric length comparator. The first reading on the test specimens was made at the age of 24h from the time of casting were mixed together. The following measurements were taken every 7 days. The average expansion of two specimens was reported.

§ 3.4.2. Test Results

The effect of gypsum addition on the expansion of Type 30 portland cement mortar cured at 23 °C is shown in Figs. 3-24 and 3-25. The plain cement mortar had no expansion. Addition of 5% gypsum increased the expansion to an ultimate value of about 0.1%. Significant expansion occurred when gypsum addition increased to 10%. The expansion then decreased as the gypsum addition was higher than 10% and finally became constant when more than 15% gypsum was added.

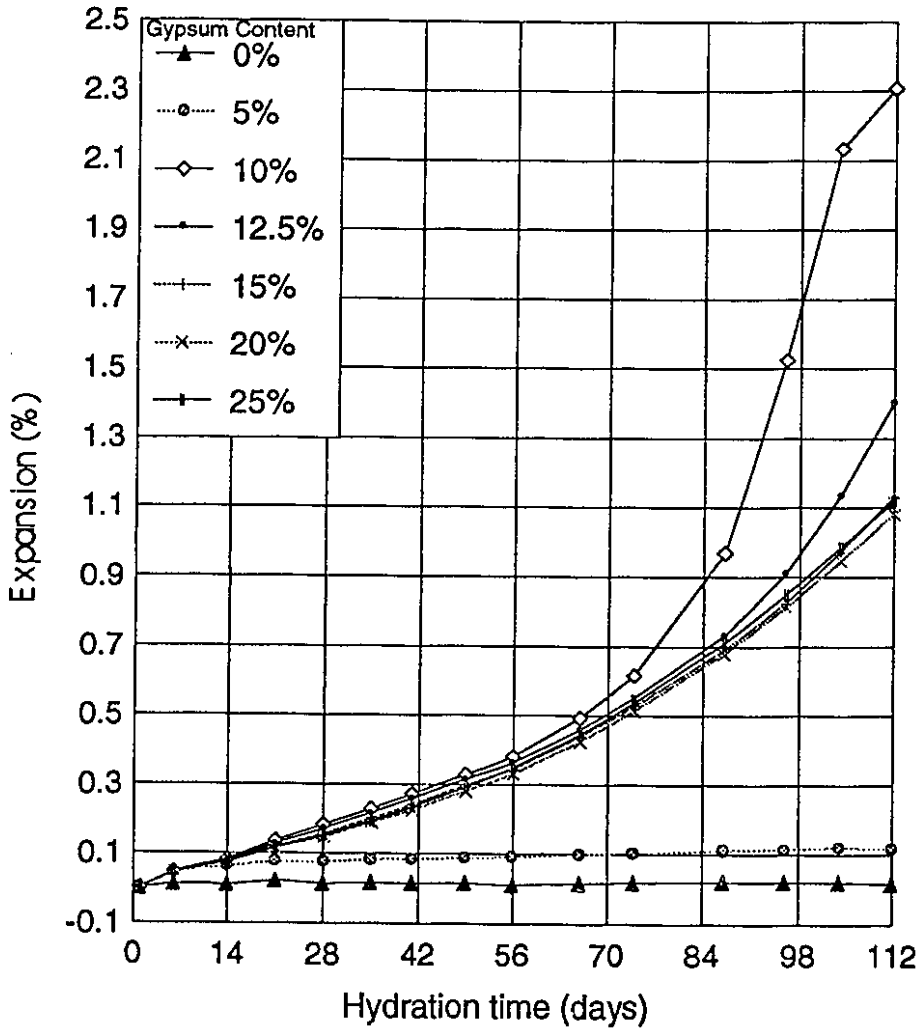


Fig. 3-24. The effect of gypsum addition on expansion development of Type 30 portland cement mortar cured at 23 °C.

The effect of gypsum addition on expansion of Type 30 portland cement mortar cured at 80 °C is shown in Figs. 3-26 and 3-27. All the specimens exhibited expansion. The expansion values of the specimens cured at 80 °C were much smaller the than the values for those cured at 23 °C when the gypsum addition exceeded 5%. The maximum expansion at 14 and 28 days occurred in the specimen with gypsum addition of 10%. The maximum at 56 and 87 days shifted to 5% gypsum content. The plain Type 30 portland cement mortar showed the largest expansion at 112 days. The addition of gypsum accelerated the expansion and reduced the ultimate expansion value at later ages. The

expansion decreased at all ages when the gypsum addition exceeded 10% and became almost constant after a 15% addition.

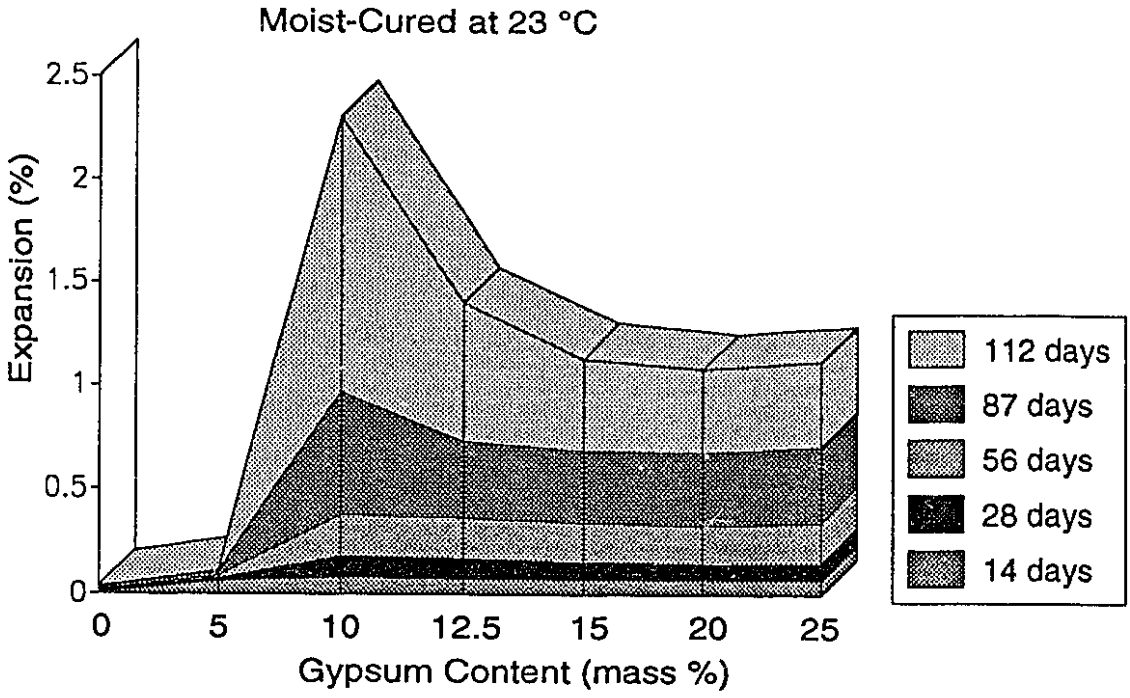


Fig. 3-25. The effect of gypsum addition on expansion of Type 30 portland cement mortar cured at 23 °C

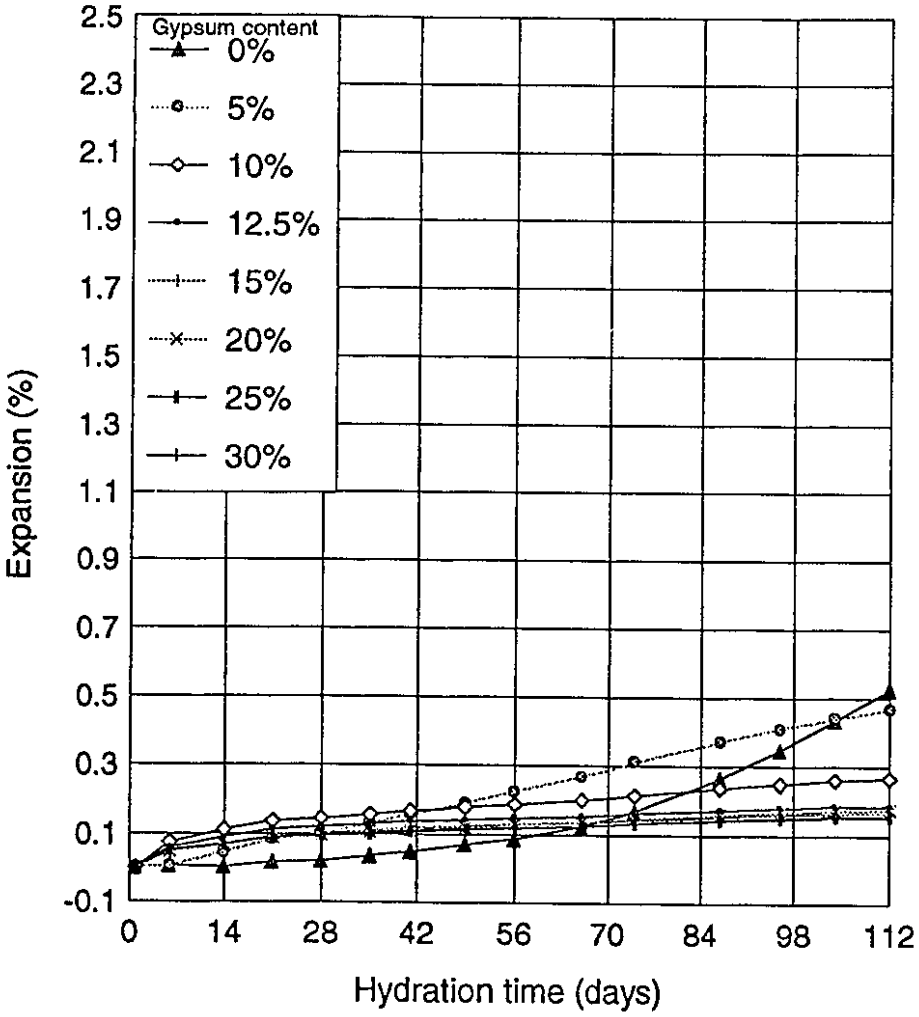


Fig. 3-26. The effect of gypsum addition on expansion development of Type 30 portland cement mortar cured at 80 °C.

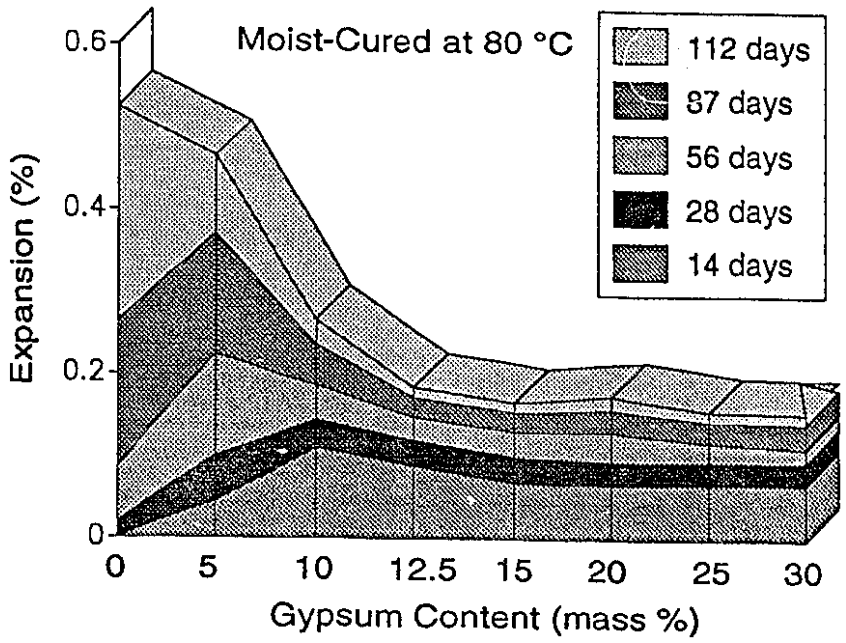


Fig. 3-27. The effect of gypsum addition on expansion of Type 30 portland cement mortar cured at 80 °C

§ 3.4.3. Discussion and Conclusion

The expansion behaviour of the portland cement mortar alters with the increase of gypsum addition. This phenomenon further illustrates the mechanisms of DEF. Sulphate adsorption by C-S-H gel significantly influences the expansion of cement mortar due to DEF. Sulphate will be adsorbed by C-S-H gel during the high temperature curing. It can be postulated that the AFm phase also forms on the surface of C_3A or its hydration products from the reaction of sulphate with aluminate phases when the cement mortar is cured at elevated temperature. Hypotheses on the effect of sulphate content in cement on the expansion characteristics can be made for three different cases according to the test results:

Case 1. A relatively small sulphate content

The sulphate will be quickly and completely adsorbed by C-S-H gel cured at high temperature at very early ages when the content of sulphate in the cement is small.

Calcium aluminate hydrates (C-A-H) form from C_3A when the sulphate is depleted. The sulphate released at later ages will react with C-A-H to form ettringite and cause delayed expansion.

Case 2. A relatively high content of sulphate but less than the sulphate adsorption capacity of C-S-H gel

More sulphate is adsorbed by C-S-H gel in Case 2 than in the Case 1 at very early ages and sulphate also reacts with C_3A or its hydrates to form the AFm phase coating on the surface of C_3A or its hydrates particles. No extra sulphate solid (i.e. gypsum) exists in the cement system after high temperature curing. The released sulphate will react with the AFm to form ettringite (AFt phase). The expansion due to ettringite formation from the AFm may be less than that due to ettringite formed directly from sulphate (e.g. gypsum). Therefore the early expansion in this case is relatively less than that in case 1. The released sulphate can react with C_3AH_6 to form ettringite at later ages after the AFm phase has been converted to the AFt phase. The more sulphate adsorbed by C-S-H gel at early ages, the higher is the expansion that can be developed at later ages.

Case 3. Sulphate content higher than the sulphate adsorption capacity of C-S-H gel

Extra sulphate solid (e.g. gypsum) will still exist in the cement system after the high temperature curing when the C-S-H gel has been saturated (about 9.8% SO_3 by mass of C_3S according to Odler, 1980) with sulphate and the AFm phase forms to the extent possible. The sulphate solid phase will dissolve under moist conditions. It directly reacts with the AFm or remaining C_3A or C_3AH_6 phases to form ettringite and causes expansion immediately after re-wetting. Since most of the Al-bearing phases (i.e. AFm, C_3A or C_3AH_6) react with the dissolved sulphate at early ages, less expansion will occur at later ages.

Chapter 4

SIGNIFICANCE OF PRE-EXISTING CRACKS ON NUCLEATION OF DELAYED ETTRINGITE IN MOIST - CURED CEMENT PASTE

- Crystal Nucleation in Cracks
- Preferential Ettringite Formation in Pre-existing Cracks

§ 4.1. Introduction

The crystal nucleation theory indicates that there is a potential for preferred nucleation at a solid surface rather than in solution in order to lower the free energy of the newly formed system (Wylie, 1952). The research based on this theory is presented to demonstrate the significance of pre-existing cracks on nucleation of delayed ettringite in moist - cured portland cement paste. A theoretical analysis of the free energy change in the nucleation process is developed from fundamental concepts and equations by Gibbs (1928) and Volmer (1939). The arguments support the view that crystals will preferentially nucleate in crack tip-zones rather than on plane solid surfaces. The effect of pre-existing crack size on crack propagation and expansion by delayed ettringite formation is also discussed in terms of the Griffith fracture theory. The results reported in this work focus on the concept of preferred nucleation in pre-existing cracks and the crack size effect on the expansion of Portland cement paste.

§ 4.2. Theoretical analysis

§ 4.2.1. Crystal Nucleation in Cracks

When the supersaturation exceeds a certain defined limit critical nuclei will form spontaneously. This behavior can be explained by the Gibbs-Thomson formula expressed in terms of supersaturation of the system, S:

$$r_c = \frac{2M\sigma}{RT\rho \ln S} \tag{4.1}$$

where, r_c is the critical radius of a spherical nucleus, σ the surface tension of the nucleus per unit area, ρ the density of the nucleus, M the molecular weight, T the absolute temperature and R the gas constant. The equation indicates that the formation of a critical nucleus is dependent on the degree of supersaturation (S) of the system. Spontaneous

nucleation is possible under supersaturation condition when the system obtains a minimum free energy.

The free energy changes during the process of nucleation may be described as follows. The over-all excess free energy, ΔG, between a small solid particle of solute and the solute in solution is equal to the sum of the surface excess free energy, ΔG_S, and the volume excess free energy, ΔG_V. Thus

$$\Delta G = \Delta G_S + \Delta G_V = 4\pi r^2\sigma + \frac{4}{3}\pi r^3 G_v \tag{4.2}$$

where G_v is the free energy change of the transformation per unit volume. The critical value, ΔG_c corresponds to the critical radius of the nucleus, r_c, and for a spherical nucleus is obtained by maximizing equation (4.2) setting $d\Delta G/dr = 0$:

$$\frac{d\Delta G}{dr} = 8\pi r\sigma + 4\,\pi r^2 G_v = 0 \tag{4.3}$$

therefore

$$r_c = -\frac{2\sigma}{\Delta G_v} \tag{4.4}$$

From equation (4.2) and (4.4):

$$\Delta G_c = \frac{16\pi\sigma^3}{3(\Delta G_v)2} = \frac{4\pi\sigma r_c^2}{3} \tag{4.5}$$

The behavior of a newly created crystalline lattice structure in a supersaturated solution depends on its size; it can either grow or redissolve, but the process which it undergoes should result in a decrease in the free energy of the particle. The critical size r_c, therefore, represents the minimum size of a stable nucleus. A crystal with a small r_c

value requires less free energy; it will therefore more readily form a nucleus than crystals with large r_c.

A spherical crystal nucleus in a crack is depicted in Fig. 4-1a. The crack is opened at an angle φ. The distance between the crack tip and nucleus is L. Two sides of the nucleus (γ) are in contact with the crack wall of the solid phase (β) and the crack is filled with supersaturated solution (α) from which nucleation occurs. The relationship between the free energy of critical nucleus formation, ΔG_{crit}, and the surface tension at different interfaces was given by Gibbs (1928):

$$\Delta G_{crit} = \frac{1}{3}(\sigma^{\alpha\gamma}A^{\alpha\gamma} + \sigma^{\beta\gamma}A^{\beta\gamma} - \sigma^{\alpha\beta}A^{\alpha\beta}) \qquad (4.6)$$

where $\sigma^{\alpha\gamma}$, $\sigma^{\beta\gamma}$ and $\sigma^{\alpha\beta}$ represent the surface tensions per unit area of interfaces and $A^{\alpha\gamma}$,$A^{\beta\gamma}$ and $A^{\alpha\beta}$ are the surface areas of the interfaces, respectively.

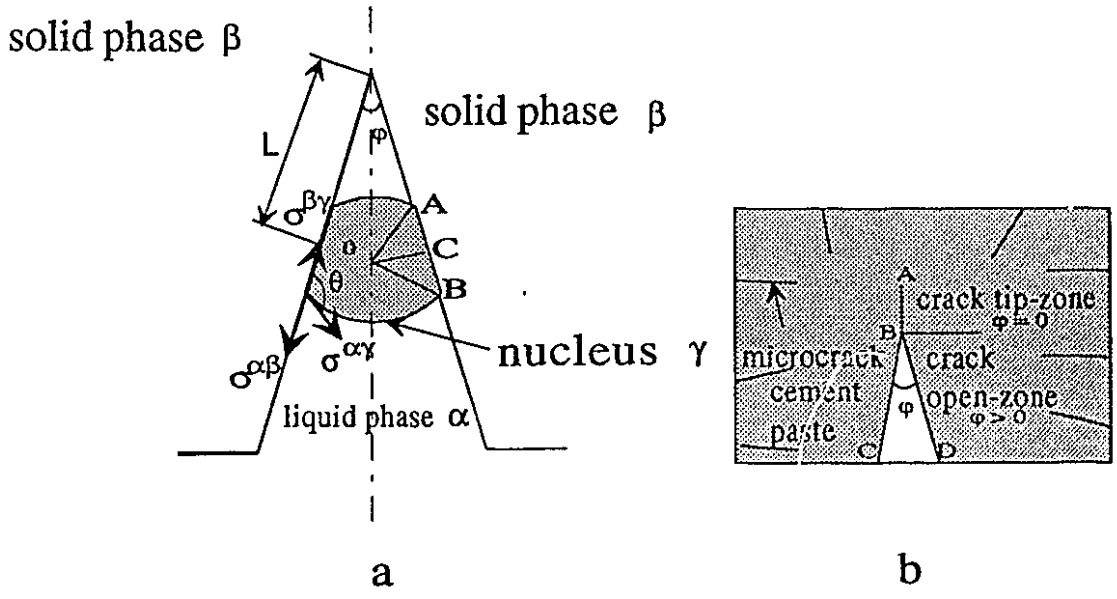


Fig. 4-1. Schematic diagram of crack in cement paste.

The surface area of spherical nucleus $A^{\alpha\gamma}$ and the areas of its circles of intersection with the crack wall $A^{\beta\gamma}$ and $A^{\alpha\beta}$ are:

$$A^{\alpha\gamma} = 4\pi r_c L \sin(\frac{1}{2}\varphi) \tag{4.7}$$

and

$$A^{\beta\gamma} = A^{\alpha\beta} = 2\pi[r_c^2 - L^2 \sin^2(\frac{1}{2}\varphi)] \tag{4.8}$$

Combining eq.(4.6), (4.7) and (4.8), we have

$$\Delta G_{crit} = \frac{2}{3}\pi r_c^2\{\frac{2\sigma^{\alpha\gamma} L}{r_c}\sin(\frac{1}{2}\varphi) + (\sigma^{\beta\gamma} - \sigma^{\alpha\beta})\,[1 - \frac{L^2}{r_c^2}\sin^2(\frac{1}{2}\varphi)]\} \tag{4.9}$$

When the crack has an angle φ tending to zero, eq. (4.9) becomes

$$\Delta G_{crit} = \frac{2}{3}\pi r_c^2\,(\sigma^{\beta\gamma} - \sigma^{\alpha\beta}) \tag{4.10}$$

The balance of surface tensions shown in Fig.4-1 results in the relationship:

$$\sigma^{\alpha\beta} = \sigma^{\beta\gamma} + \sigma^{\alpha\gamma}\cos\theta \tag{4.11}$$

where θ is the contact angle between the crystal nucleus and the crack wall. By combining eq.(4.10) and (4.11), the critical free energy of the newly created system is equal to:

$$\Delta G_{crit} = -\frac{2}{3}\pi r_c^2\,\sigma^{\alpha\gamma}\cos\theta \tag{4.12}$$

The critical free energy for a nucleus forming on a plane solid surface was given by Volmer (1939):

$$(\Delta G_{crit})_{plane} = \frac{2}{3}\pi r_c^2\,\sigma^{\alpha\gamma}\,(1 - \cos\theta - \frac{1}{2}\cos\theta\sin^2\theta) \tag{4.13}$$

A comparison of free energies based on eq.(4.12) and eq.(4.13) leads to the following expression:

$$(\Delta G_{crit})_{plane} - \Delta G_{crit} = \frac{2}{3}\pi r_c^2 \sigma^{\alpha\gamma} (1 - \frac{1}{2}\cos\theta \sin^2\theta) > 0$$

It follows that nuclei will preferentially form in cracks as ΔG_{crit} is less than $(\Delta G_{crit})_{plane}$.

A crack in cement paste can be depicted as containing a crack tip-zone and a crack open-zone ("AB" and "CBD" in Fig.1b, respectively). The crack angle φ in the tip-zone tends to zero. In most cases, the initial cracks, d5e to drying shrinkage, fatigue or mechanical stress, have a tip-zone. If the supersaturation condition of the solution in the cement paste is met, i.e. the requirement for critical nucleation of ettringite crystals as described in eq.(4.1), nucleation must first occur in the crack tip-zone, where the lowest free energy conditions exist. Once the nuclei in the tip-zone are stable, the driving force of supersaturation results in the growth of ettringite crystals and subsequent opening of the crack. The crack tip (point "A" in Fig.4.1b.) then extends into the cement paste matrix. The newly extended crack tip-zone can be the next preferred position for nucleation. The cracking-nucleation degradation cycles will continue until the material is totally damaged, if the supersaturation condition is maintained.

In the crack open-zone, the preferred position of nucleation is mainly dependent on the contact angle (θ, in Fig.4-1a.) of newly formed nuclei on the cement paste surface. If the angle θ is less than 90° surface tension of the nuclei will be lowered and nucleation will occur in the crack; if the angle is larger than 90° the nuclei may tend to form in the bulk solution. These cases are dependent on the extent to which the width of the crack after opening is larger than the diameter of the nuclei. The free energy change of the nucleation in the crack open-zone (as opposed to crack - tip) is in fact equal to that on the plane solid surface (eq.4.13), if the diameter of the nuclei is less than the crack width.

It can be deduced from the above analysis that nucleation of ettringite crystals in cement pastes will preferentially occur in crack tip-zones rather than cement matrix under conditions of supersaturation. Growth of ettringite crystals in the crack will cause the extension of the crack and subsequently damage the concrete.

§ 4.2.2. Crack Size Effect

In addition to delayed ettringite formation, the expansion of cement paste depends also on the fracture characteristics of the solid. Cracks exist for many reasons in the cement paste matrix. Drying shrinkage is one of the most common sources. Once the crack is formed, delayed ettringite will preferentially grow in it. Expansion develops and cracks propagate in a direction perpendicular to the expansive force.

In cement paste, microcracks are surrounded by the hydrated cement matrix. It is assumed that the brittle cement matrix has uniform fracture characteristics and that linear elastic fracture mechanics principles apply. The cement paste sample is considered to consist of finite units each containing one microcrack. According to Griffith (1921), the condition of crack propagation in one unit at the critical state is:

$$G = G_f \tag{4.14}$$

where in this case G is the fracture energy generated from delayed ettringite formation; G_f is the energy needed to initiate a fracture. The value of G_f is approximately constant and can be considered a material property. If $G < G_f$, the crack cannot propagate, that is, no expansion occurs. The crack begins to propagate and expansion occurs when $G > G_f$. The fracture energy G can be expressed in terms of the stress intensity factor resulting from the expansion pressure:

$$G = \frac{K_I^2}{E} \tag{4.15}$$

where E is Young's elastic modulus.

The stress intensity factor is dependent on expansion pressure and a function f(α) related to crack size and specimen or unit geometry. It can generally be expressed in the form:

$$K_I = \frac{P}{b\,d}\sqrt{\pi\, a}\, f(\alpha) \tag{4.16}$$

where P is expansion force due to delayed ettringite formation; b and d are dimensional factors; a is the size of pre-existing crack; f(α) is a nondimensional function of the relative crack length.

In cement paste, the development of fracture energy around a cracked area is dependent on the expansion pressure and existing crack size. Once the fracture energy G reaches the value of G_f, crack initiation and propagation, are accompanied by expansion. The expansion pressure is released as soon as the crack is opened. The term G then reduces to less than G_f. Further expansion requires additional ettringite formation. Inspection of eq.(4.16) , indicates that a larger size crack requires less expansion pressure (e.g. less ettringite formation) to produce a critical fracture energy state. Similarly a larger size crack will result in higher expansion for the same expansion pressure.

§ 4.3. Experimentation

§ 4.3.1. Materials

Type 10 Portland cement with the following oxide composition (mass%) was used: SiO_2=19.83; CaO=61.21; Fe_2O_3=3.20; Al_2O_3=4.18; MgO=4.09; SO_3=3.93; Na_2O=0.45 and K_2O=0.82.; the mineral composition (mass%) is: C_2S=15.78; C_3S=54.55; C_3A=5.67; C_4AF=9.73. Pure C_3A (3%) and gypsum (2%) were added to the cement in experiments designed to optimize conditions for delayed ettringite formation.

§ 4.3.2. Specimen Preparation

Type 10 Portland cement was mixed with 3% pure C_3A and 2% gypsum in a rotating bottle for 48 hours to optimize conditions for delayed ettringite formation. The cement was mixed with water in a high speed mixer for one minute. The water-cement ratio of the cement paste was 0.5. The sample was cast in 30 mm diameter plastic bottles. Three curing conditions were used in the first 24 hours: (1) normal temperature moist curing (23 °C and 100% r.h.) for 24 hours; (2) moist curing with a heating rate equal to 0.8 °C/min for 1.35 hours followed by curing at 65 °C for 6 hours and cooling at ambient for an additional 6 hours, and then normal temperature moist curing (23 °C and 100% r.h.) for 12 hours; (3) moist curing with a heating rate equal to 0.8 °C/min for 1.5 hours followed by curing at 95 °C for 6 hours and cooling for 6 hours, and then normal temperature moist curing (23 °C and 100% r.h.) for 12 hours. The sample cylinders were then demoulded. All hardened cement pastes were cut into 3 mm thick discs. The pre-existing cracks were manufactured by following the procedures outlined in Table 4. Subsequent treatments for each sample are also listed in Table 4. Samples were then mounted in Tuckerman optical strain gages to determine expansion. The samples with strain gages were placed in lime water at room temperature. Readings were taken at designated times after 28-days hydration to avoid the possibility of any extraneous effects on hydration at early age due to the different sample preparation procedures.

Compacted cement samples which have similar microstructure were also prepared to demonstrate the effect of pure constituents of hydrated cements on expansion potential at different curing temperatures. The constituents of these samples were the same as those prepared by the procedures outlined in Table 4. The hydrated cement paste samples were ground into powders with particle size similar to Portland cement. The samples were compacted under 100 MPa pressure in a steel mould. This was followed by curing

in lime water for 28 days. The compacts were subsequently mounted in optical strain gages to measure the expansion.

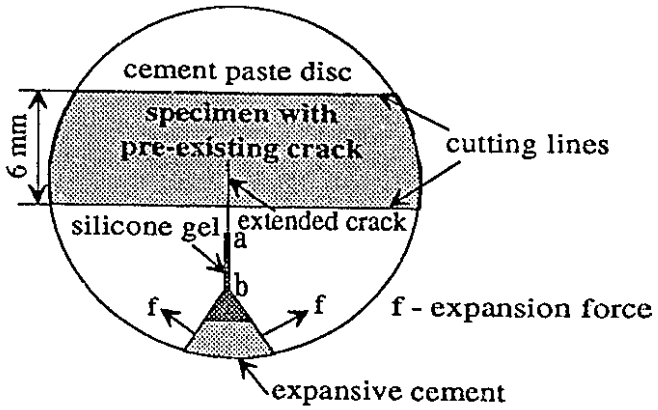


Fig. 4-2. Cement paste specimen with pre-existing crack.

Table 4.1. Preparation of Specimens

Specimen	Treatment after First 24 Hours Curing
Control	Control: continuously cured in lime water.
Crack Preparation	A "Y" cut was made in the cement paste disc; the crack tip ("ab" in Fig.4-2.) was sealed with silicone sealant to avoid the ingress of foreign ions into the crack tip; the remaining cavity in the "Y" cut was filled with expansive cement paste; the specimens were subsequently moist cured until crack growth into the matrix of the cement paste disc was evident; the samples were then cut into pieces about 2 x 5 x 30 mm (see shaded area in Fig.4-2), and cured in lime water at 23°C.
85 °C dry	After the first 24 hours of curing, the sample is dried at 85 °C in an oven for 24 hours, and then cured in lime water at 23 °C.
85°C dry+Crack	A crack is prepared as described above and then the specimen is dried at 85 °C after the first 24 hours curing.
23 °C dry	After first day curing, the sample is dried at room temperature for 24 hours (23 °C & 50% R.H.), and then cured in lime water at 23 °C.
Vacuum dry	Vacuum dry: After the first 24 hours of curing, the sample is dried at room temperature in vacuum for 24 hours, and then cured in lime water at 23 °C.

The samples with a pre-existing crack were immersed in 2-propanol after about 90 days hydration and then dried under vacuum for 24 hours. The samples were then intentionally fractured along the crack and beyond. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) were performed on material from the crack surface and the cement paste matrix. SEM micrographs were obtained using a Cambridge Stereoscan S250.

§ 4.4. Results

The effect of the prescribed treatments on the expansion of normal temperature moist cured cement paste is shown in Fig. 4-3. The specimens that were subjected to drying had a slightly higher expansion than those without drying. In general the expansion value was small and less than 0.01%. The effect of the prescribed treatments on the expansion of cement paste moist-cured at 65 °C is shown in Fig. 4-4. The combined effect of pre-cracking and drying at 85°C resulted in larger expansion (about 0.02% at 72-days hydration) than the other specimens. Drying after the first day curing enhanced expansion for all the samples. The higher drying temperature resulted in greater expansion. The effect of the treatments on the expansion of 95 °C moist-cured cement paste is shown in Fig. 4-5. The combined effect of pre-cracking and drying at 85 °C was similar to the behavior of the cement paste moist-cured at 65 °C. A significant expansion larger than 0.03% resulted. The specimen treated by drying at 85 °C had much less expansion than the afore-mentioned but higher than the others. Pre-cracking alone did not have an obvious effect on the expansion of cement paste without the drying treatment.

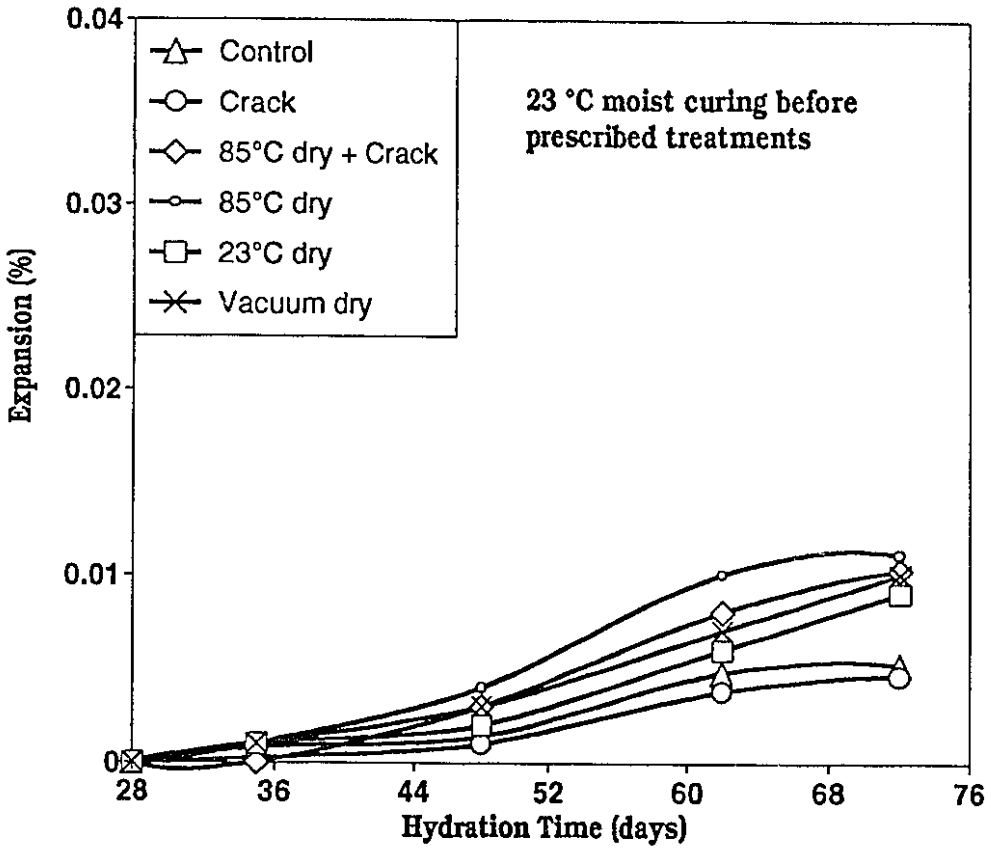


Fig. 4-3. Effect of prescribed treatments (Table 4.1) on the expansion of cement paste moist cured at 23 °C.

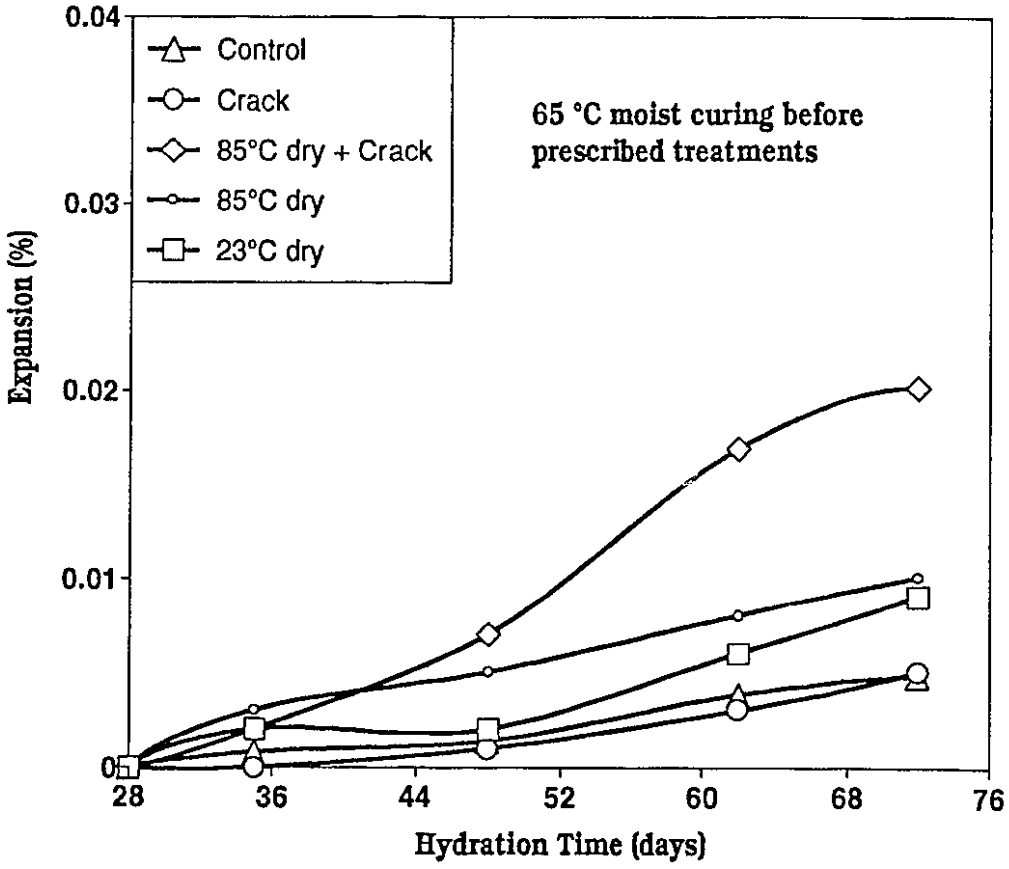


Fig. 4-4.Effect of prescribed treatments (Table 4.1) on the expansion of cement paste moist cured at 65 °C.

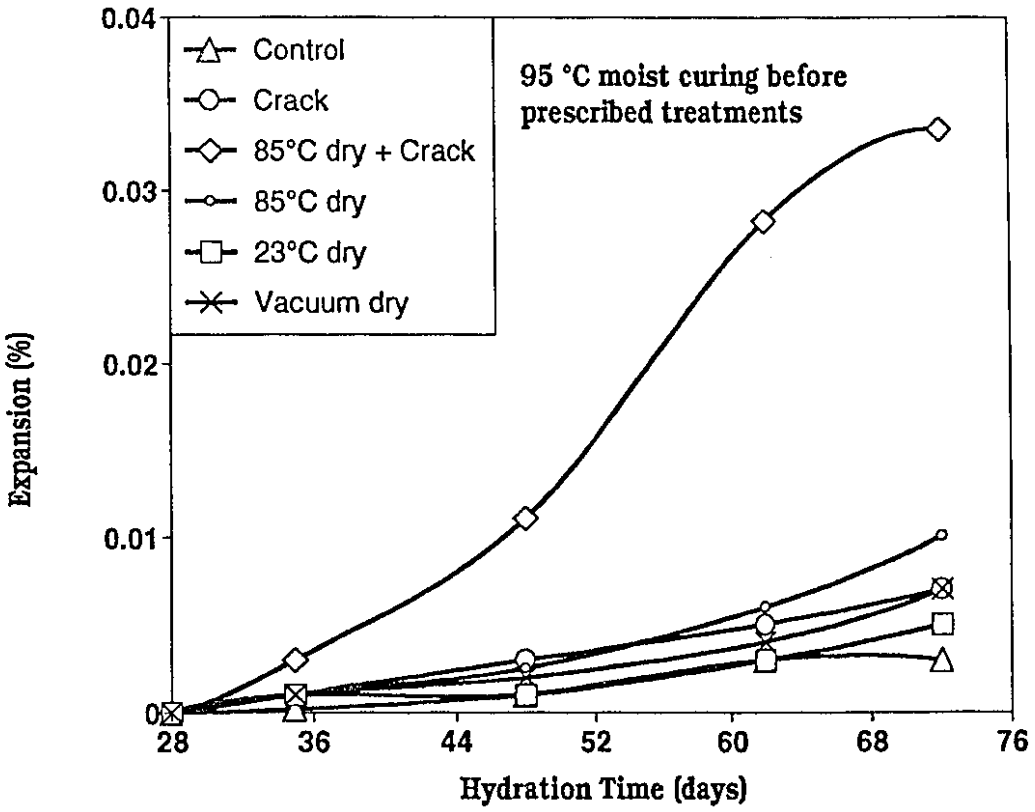


Fig. 4-5. Effect of prescribed treatments (Table 4.1) on the expansion of cement paste moist cured at 95 °C.

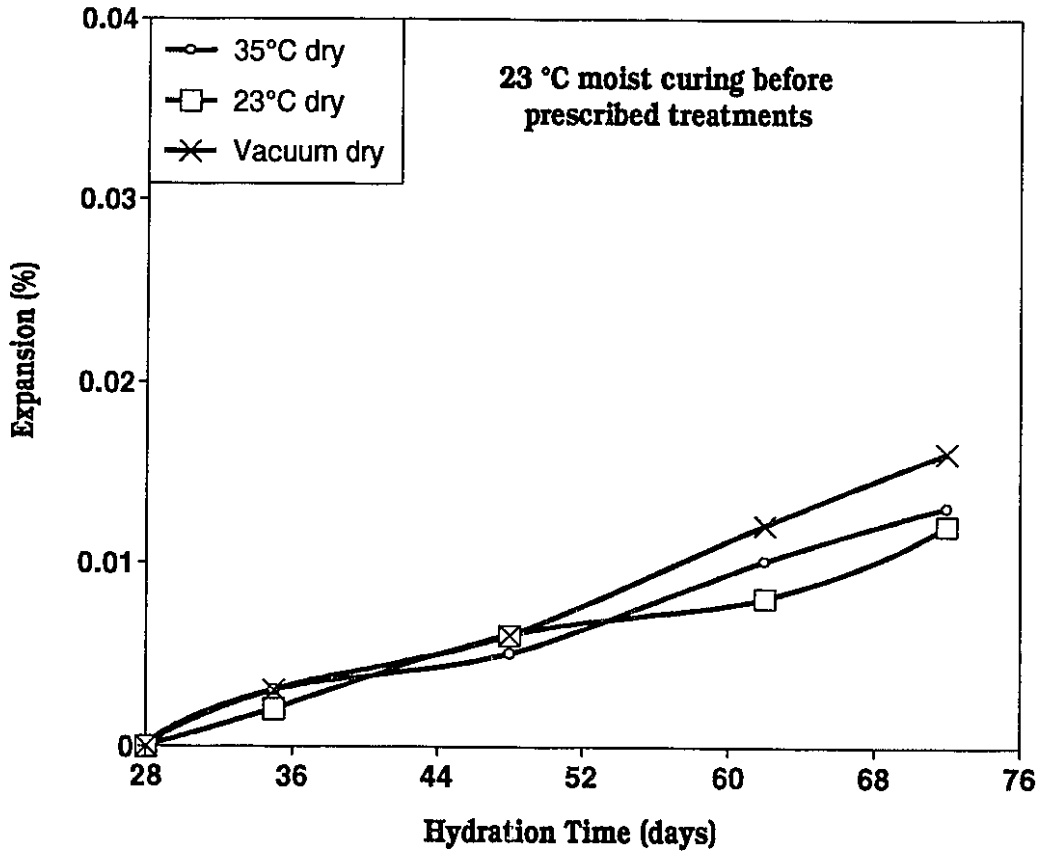


Fig. 4-6. Effect of prescribed treatments (Table 4.1) on the expansion of cement compacts moist cured at 23 °C.

The effects of the prescribed treatments on expansion of compacts after room temperature moist curing, 65 °C moist curing and 95 °C moist curing are shown in Fig. 4-6, 4-7 and 4-8 respectively. The expansion of the compacts is mainly due to differences in the chemical and mineral composition of the 1-day hydrated cement paste subjected to different curing conditions and the prescribed treatments. The expansion values of the compacts with the materials treated in different ways were similar for the samples moist cured at room temperature and moist-cured at 65 °C. The expansion values reached about 0.015% at 72-day hydration. Expansion values were obviously higher and developed earlier for the sample with 95 °C moist curing than those with lower temperature curing. Higher temperature drying (85 °C) caused large expansions up to 0.02%.

SEM micrographs of the pre-existing crack surface and cement matrix in the sample moist-cured at 95 °C are shown in Fig. 4-9a. and 4-9b. respectively. An SEM picture of the crack surface of the room-temperature cured sample is shown in Fig. 9c. Highly concentrated needle-like crystals were commonly found on the crack surfaces of cement paste. These crystals were identified as ettringite by EDXA. The crack surface of the specimen that was subjected to moist curing at 95 °C followed by prescribed drying treatment was completely covered with ettringite. The ettringite crystals growing in the crack were much larger than those normally found in Portland cement paste, or an expansive cement paste matrix. Ettringite crystals were only occasionally detected in randomly selected areas of the bulk paste (Fig. 4-9b.). No ettringite was detected on the pre-existing crack surface of the specimen that underwent normal temperature curing (Fig. 4-9c).

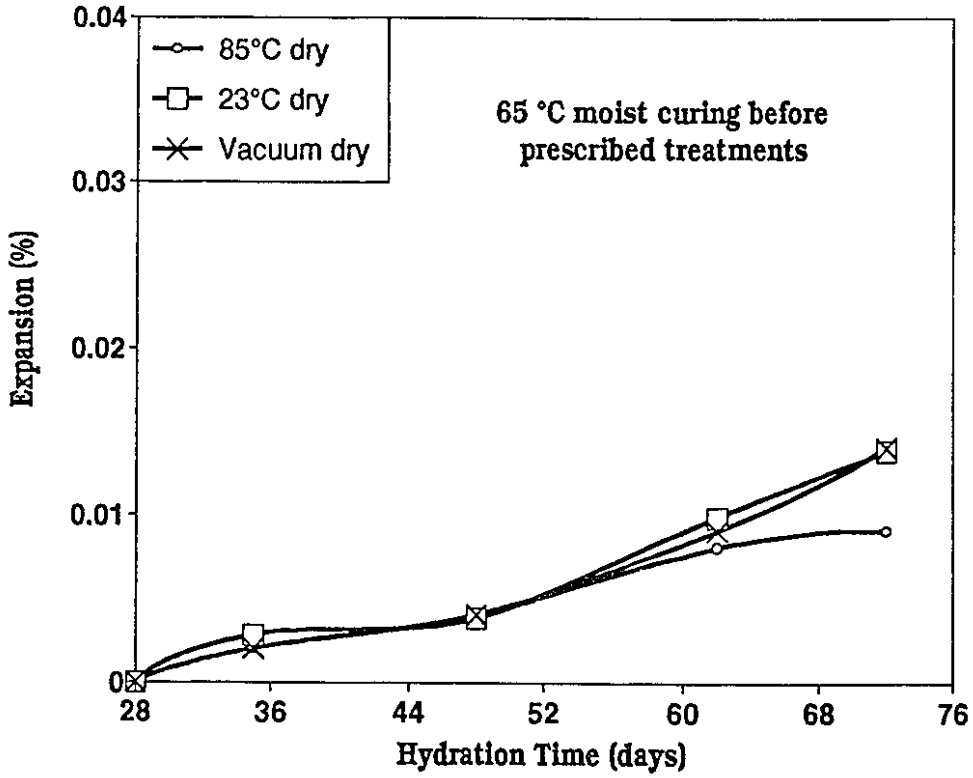


Fig. 4-7. Effect of prescribed treatments (Table 4.1) on the expansion of cement compacts moist cured at 65 °C.

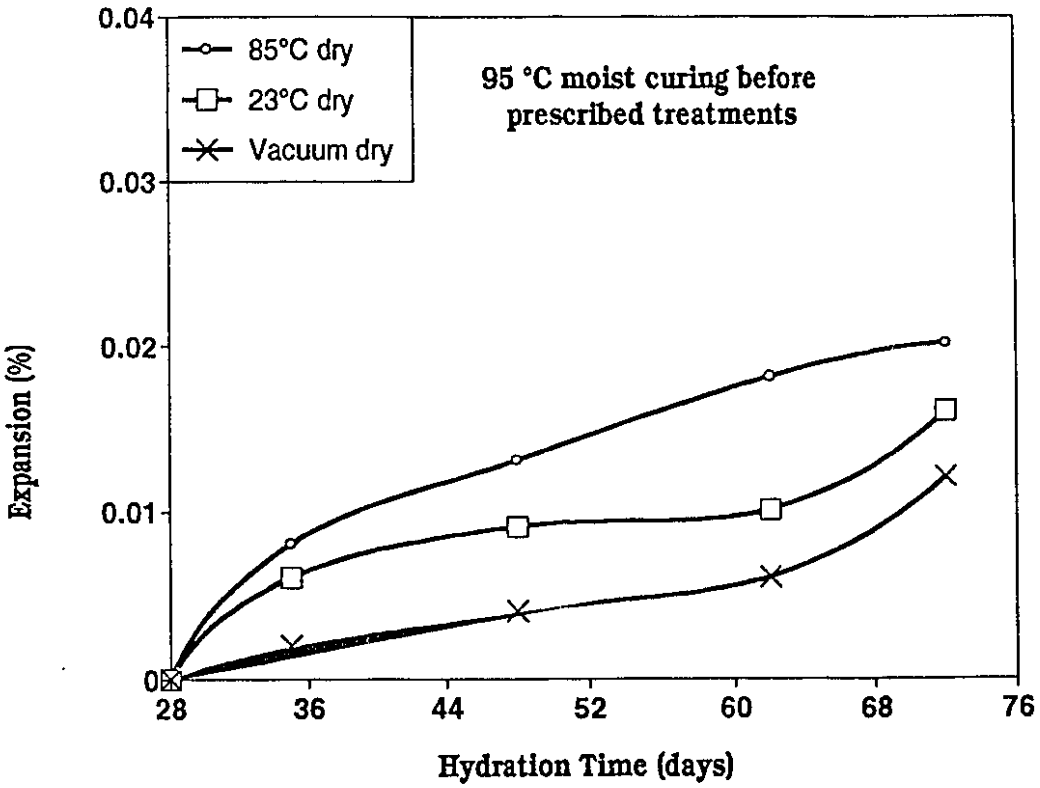


Fig. 4-8. Effect of prescribed treatments (Table 4.1) on the expansion of cement compacts moist cured at 95 °C.

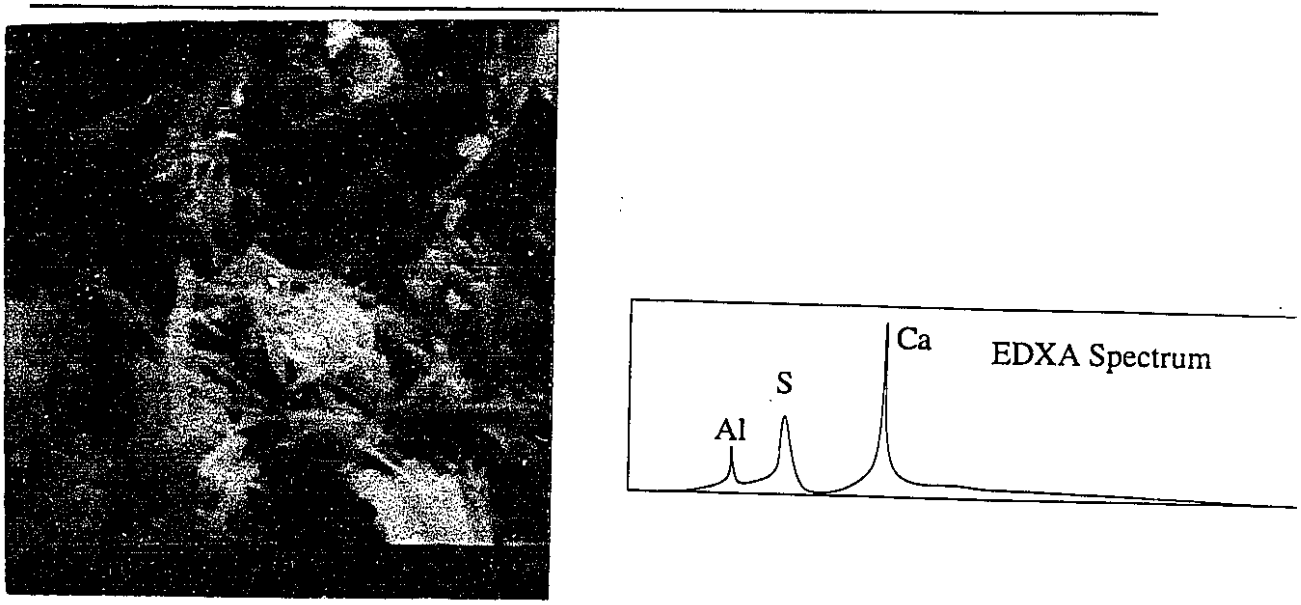


Fig. 4-9a. SEM/EDXA analysis on a pre-existing crack surface of Portland cement paste moist-cured at 95 °C.

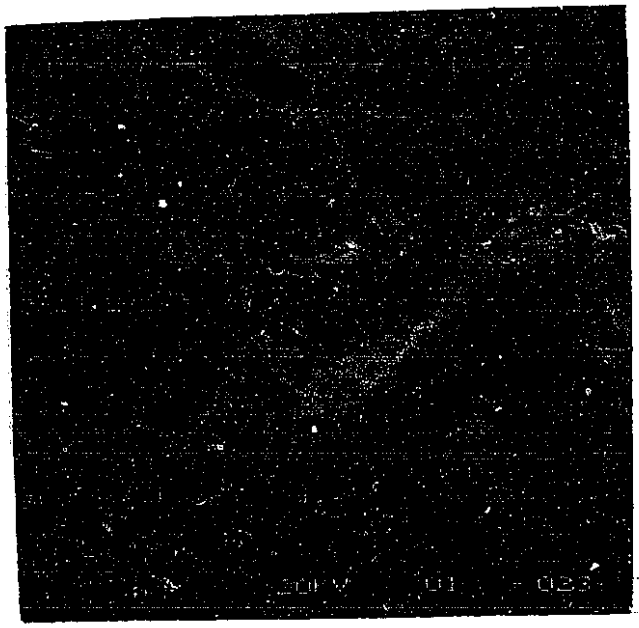


Fig. 4-9b. SEM micrograph of the Portland cement paste matrix distant from the crack surface moist-cured at 95 °C.

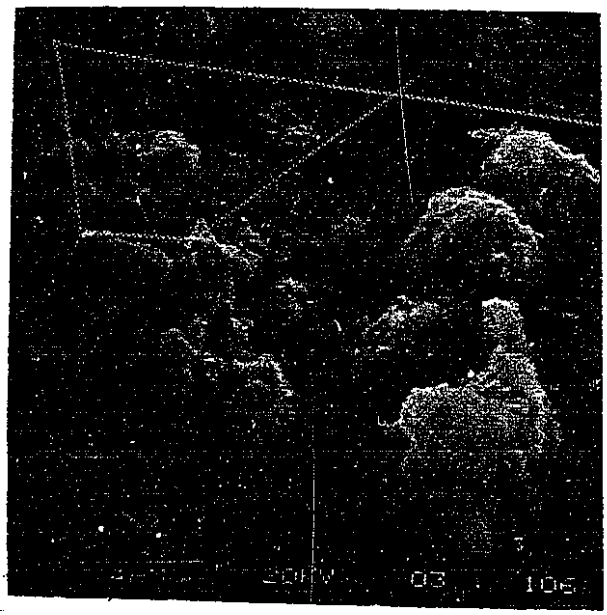


Fig. 4-9c. SEM micrograph of a pre-existing crack surface of normal temperature cured Portland cement paste.

§ 4.5. Discussion

§ 4.5.1. Curing Temperature

It follows from e.q. (4.1) that the critical radius of certain crystal nuclei formed from solution at constant temperature is dependent on the supersaturation of the solution. The essential condition for crystal nucleation of delayed ettringite is the dissolution of sufficient reactants, i.e. alumina, sulphate and calcium, in the cement solution to obtain supersaturation. High temperature moist curing (above 75 °C) appears to provide a satisfactory environment for "delayed ettringite formation. This has been attributed to the transformation of monosulphate to ettringite due to variation in stability at different temperatures (Heinz and Ludwig, 1987), and to the release of sulphate from C-S-H gel (Copeland et al. 1967). They were only able to detect ettringite by XRD analysis in the system C_3A-$CaSO_4$·$2H_2O$-$Ca(OH)_2$-H_2O at 95-100°C. No monosulphate was observed. It appears that the stability of the sulphoaluminate phase may also be dependent on the concentration of the reactants involved in the reaction. High temperature moist curing plus high temperature drying results in greater expansion of compacted systems and formation of delayed ettringite. Release of sulphate from C-S-H gel may be possible when cement paste is hydrated at high temperature, but further experimental evidence is required. Drying after moist curing possibly accelerates the release of sulphate. Post-cracking behavior of high temperature moist-cured cement paste would indicate that high temperature moist curing is a critical condition for "delayed ettringite formation and subsequent deterioration.

§ 4.5.2. Pre-existing Cracks

The free energy analysis described earlier may apply when moist curing at 95 °C. Nucleation occurs preferentially in the crack tip-zone when satisfactory conditions including sufficient supersaturation for delayed ettringite formation occurs. The nucleus formed in the crack tip-zone (model Fig. 4-1a) must have two surfaces in contact with

the crack wall to lower the free energy. Further growth of the crystal in this limited space will likely act as a source of crystallization pressure. The crack extends when the stress intensity at the crack tip exceeds a critical value. The width of crack increases with the growth of ettringite crystals and becomes larger than the critical radius of the nucleus. Additional nucleation sites will form in the new crack tip-zone following the crack extension. Continuous growth of the crack by this mechanism is possible if supersaturation is maintained.

§ 4.5.3. Drying

Shrinkage is a main source of microcrack formation contributing to deterioration by delayed ettringite formation. It can be hypothesized that during the drying-wetting process irreversible shrinkage reduces the effective space for ettringite crystal growth, resulting in greater expansion. Sulphate in C-S-H gel may possibly be released during drying. Therefore the drying process may produce conditions favorable for deterioration of paste by delayed ettringite formation. Drying has been shown to result in significant expansion of high temperature moist-cured Portland cement paste.

§ 4.5.4. Crack Size Effect

Crack initiation and propagation in accordance with the Griffith theory [10] is dependent on the pre-existing crack size. Greater expansion will result when the existing crack in the cement paste is larger. The expansion - crack-opening process in hardened cement paste is different from the fracture process of a specimen under constant load. During the crack opening process, expansion pressure is released, and the fracture energy in the material is reduced to a value less than critical fracture energy. Further expansion requires further ettringite formation to create additional expansion pressure at a new critical state. In the experiment described previously, the size of the prepared crack was much larger than those created from the drying process. The opening of such a crack requires much less energy than a typical shrinkage microcrack. The opening of cracks

proceeds with expansion perpendicular to the direction of crack growth. Crack propagation requires high energy when the microcracks are less than a certain size. Significant deterioration by delayed ettringite formation may possibly be attributed to pre-existing larger size cracks similar to those present in the transition zone.

§ 4.6. Conclusions

1. Nucleation of crystals in cement pastes including ettringite will preferentially occur in crack tip-zones rather than on plane solid surfaces under conditions of supersaturation.
2. Crack growth and nucleation of ettringite will continue, if supersaturation is maintained.
3. High temperature moist curing, followed by high temperature drying of cement paste containing pre-existing cracks are critical conditions for deterioration by delayed ettringite formation.
4. Larger pre-existing cracks are predominantly responsible for higher expansion when conditions for delayed ettringite formation are optimum.
5. Highly concentrated large size ettringite crystals can be commonly found in cracks of high temperature moist-cured Portland cement paste when drying occurs after moist curing.

Chapter 5

A THROUGH SOLUTION MECHANISM FOR DELAYED ETTRINGITE FORMATION IN PRE-EXISTING CRACKS IN PORTLAND CEMENT MORTAR

- Demonstration of Preferential Ettringite Formation in Pre-Existing Cracks
- A Through Solution Mechanism

§ 5.1. Introduction

It has been inferred from crystal nucleation theory that there is a potential for preferred nucleation at a solid surface rather than in solution in order to lower the free energy of the newly formed system. Research based on this theory has been reported to demonstrate the significance of pre-existing cracks on nucleation of delayed ettringite in cement paste moist-cured at elevated temperature. A recent study by Scrivener and Taylor (1993) appears to confirm this phenomenon. It was suggested that high temperature moist curing followed by high temperature drying to form microcracks was an optimum condition for concrete deterioration due to delayed ettringite formation. Crystals preferentially nucleate in crack tip-zones rather than on plane solid surfaces.

Two different arguments were examined for interpretation of ettringite related expansion mechanisms for Portland cement concrete: the crystal growth theory and the swelling theory. Cohen and Richards (1982) postulated that expansion results from the growth of ettringite crystals formed on the surfaces of Al-bearing particles. The growth of these crystals results in crystallization pressure and expansion occurs. Mehta (1973) argued that expansion is attributed to the swelling of colloidal particles of ettringite. The formation of this swelling gel occurs by a through-solution mechanism. Expansion could occur either by intercalation or surface adsorption effects. The phenomenon of preferred nucleation of delayed ettringite in pre-existing cracks appears to support arguments for a through-solution deposition mechanism. Resulting expansion likely occurs through crystal growth in conformance with Cohen's postulation.

This chapter attempts to provide a comprehensive discussion of the mechanisms of delayed ettringite formation. Further evidence in support of a previously reported study on nucleation characteristics of delayed ettringite in cracks of portland cement paste is reported. Test results presented here indicate that the reactants for delayed

ettringite formation in cracks can come from sources away from the cracks. Diffusion of reactant ions through the concrete pore solution appears to be a key element of the process responsible for initiation of delayed ettringite nucleation in cracks.

§ 5.2. Experimentation

§ 5.2.1. Materials

Type 50 Portland cement: supplied by Lafarge Canada Inc. Chemical composition (mass%) is: SiO_2=23.18; CaO=56.77; Fe_2O_3=4.12; Al_2O_3=5.19; MgO=3.64; SO_3=2.76; Na_2O=1.08 and K_2O=0.52.

Triclinic tricalcium silicate (C_3S): supplied by Construction Technology Laboratories, Skokie, Illinois, U.S.A.

Hydrated triclinic tricalcium silicate (Mixture of CH and C-S-H gel): C_3S was hydrated in excess water until the presence of anhydrous C_3S mineral could not be detected by XRD analysis. The hydrated C_3S was ground in acetone to similar fineness as Portland cement (amount passing 75-μm sieve was equal to 97.87%, ASTM C 184-90). It was dried at 65°C for 24 hours.

Tricalcium aluminate (C_3A): supplied by Construction Technology Laboratories, Skokie, Illinois, U.S.A.

Reagent grade gypsum ($CaSO_4 \cdot 2H_2O$): supplied by Anachemia Canada Inc.

Reagent grade aluminium sulphate ($Al_2(SO_4)_3 \cdot 14H_2O$): supplied by Anachemia Canada Inc.

Reagent grade calcium hydroxide ($Ca(OH)_2$): supplied by Anachemia Canada Inc.

Sand: Graded standard sand meeting ASTM C 778 requirements was used.

§ 5.2.2. Sample Preparation

The specimen design is shown in Fig. 5-1. The specimens were prepared in the following way: a *cement mortar core* assumed to contain little or no ettringite (see Fig.

5-7a) was enclosed in a *cement mortar enclosure* to which ettringite was added or formed. The mortar core was first cast in the shape of a 50x50x250 mm prism using Type 50 Portland cement and graded standard sand (ASTM C 778). The water-cement ratio was 0.5 and the cement-sand ratio was 1:2.75. A crack was carefully prepared by bending the prism specimen. The load was slowly increased until the crack extended about 3/4 of the specimen height. The specimen was then cut at a distance of 10 mm on each side of the crack. The thickness of the specimen was 20 mm. The specimen was sealed with epoxy at each end as shown. The mortar enclosure was made with the same material as the mortar core. Different additives, however, were incorporated into the mortar mixture to provide a source of ettringite. The additives are listed in Table 5.1. The mortar enclosures were mixed 28 days after the mortar cores. A mortar core hydrated 28 days with a prepared crack was embedded in each of the fresh mortar enclosures prepared with a different formulation. The crack mouth was placed above the surface of fresh mortar so that the crack would not be contaminated by ettringite. The composite specimen (core + enclosure) was cast in a 50x50x50 mm mould. The specimens were demoulded after 24 hydration. The specimens were immersed in lime water up to 4/5 of the height of the specimens. The open mouth of the crack was kept out of the lime water. The ions could only diffuse into the crack from the two sides perpendicular to the crack. An optical strain gage was mounted across the crack mouth. The dimensional change due to the opening of the crack mouth was recorded. The crack mouth opening was attributed to ettringite formation in the crack. In addition to the preparation of cubic specimens with a cracked ettringite-free core, specimens made from only mortar enclosure material were also cast as prisms, 25x25x125 mm (M-1, Table 5.1). The length change was recorded from 1 to 180 days. XRD and SEM/EDXA analysis were conducted on the crack surface after 180 days hydration.

Table 5.1. Additives for Mortar Enclosure in Test Specimens

Specimen Designation	Additives (mass % of cement)
M-1	None
M-2	ettringite mixture I* (5%)
M-3	ettringite mixture II** (5%)
M-4	C_3A (10%) + gypsum (5%)
M-5	$Al_2(SO_4)_3$ (3%) + $Ca(OH)_2$ (2%)

* *It was prepared at 85 °C. The stoichiometric amount of reagent aluminium sulphate and calcium hydroxide required for ettringite formation was mixed with sufficient distilled water in a sealed plastic bottle. The mixture was reacted at 85 °C in a water bath for 30 days. The wet mixture was then vacuum dried for 48 hours.*

** *It was prepared at 23 °C. The reactants and the preparation procedure were the same as the Ettringite mixture I.*

§ 5.3. Results

Delayed ettringite formation in pre-existing cracks in Portland cement mortar

The expansion values of the enclosure mortars and mortar cores are shown in Figs. 5-2 to 5-6. It is apparent that little expansion occurred in the enclosure mortar specimens containing prepared ettringite (M-2 and M-3) and the control specimen. Expansion resulted at early ages only (before 14 days) for the enclosure mortar specimens containing reactants required for *in-situ* formation of ettringite.

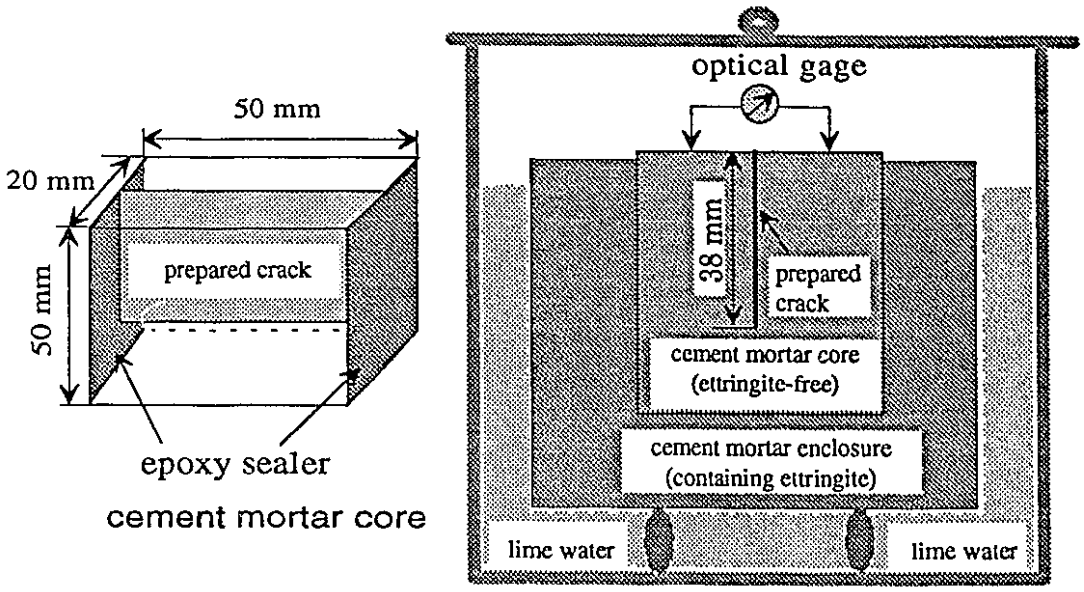
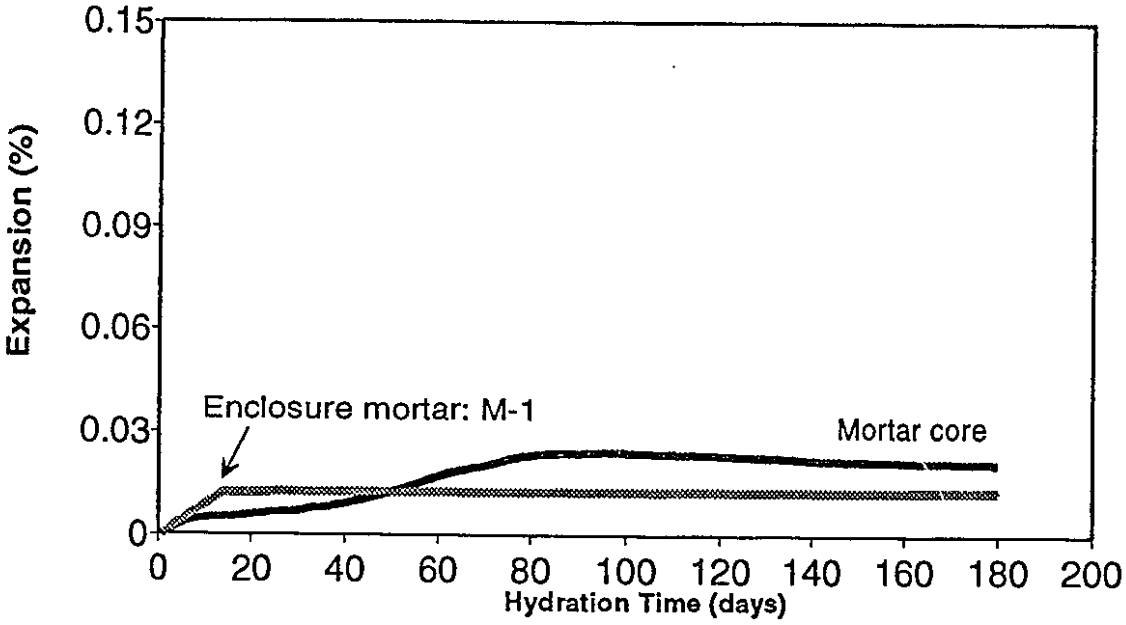


Fig. 5-1. Schematic diagram of test specimens.

Expansion at the crack mouth opening of the mortar cores was significantly different than for the mortar enclosures in the same cores. No significant expansion was found for the control sample (M-1, Fig. 5-2) and the specimen containing ettringite prepared at 23 °C (M-3, Fig. 5-4). The specimen containing ettringite prepared at 85 °C (M-2, Fig. 5-5) started to expand appreciably after 60 days. Its expansion was about 0.13% at 180 days. The specimens M-4 (Fig. 5-5) and M-5 (Fig. 5-6) expanded much earlier than specimen M-2. The expansion started to accelerate at about 40 days. Their ultimate expansion values at 180 days were 0.09% and 0.11% for M-4 and M-5 respectively.

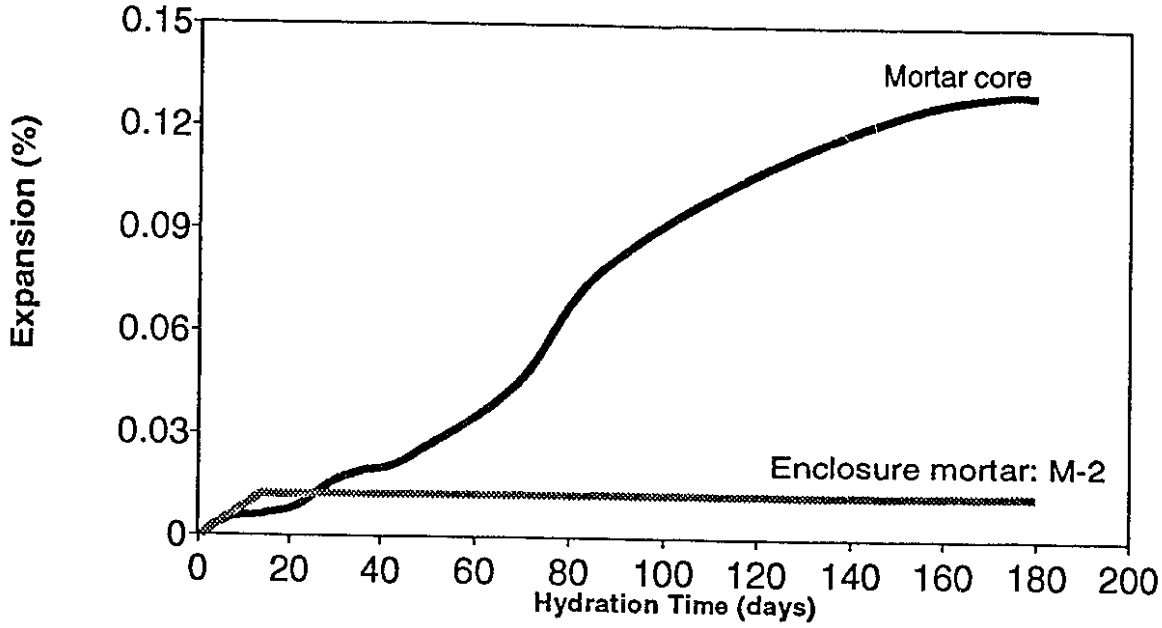
Results of x-ray diffraction analysis (XRD, Rigaku X-Ray Diffractometer System Geigerflex D/Mas -B), scanning electron microscopy and energy dispersion x-ray analysis (SEM/EDXA, Cambridge Stereoscan S250) of materials on the crack surface are

shown in Fig. 5-7. Ettringite is clearly identified in the XRD spectrum at a d-spacing of 0.98 nm. It appears to co-exist with the calcium silicate hydrates (EDXA spectrum). A sulphur peak and an aluminium peak correspond to the presence of ettringite. This ettringite is believed to be responsible for the extension of the crack mouth described above.



Specimen Designation	Additives (mass % of cement)
Mortar Core	None
M-1	None

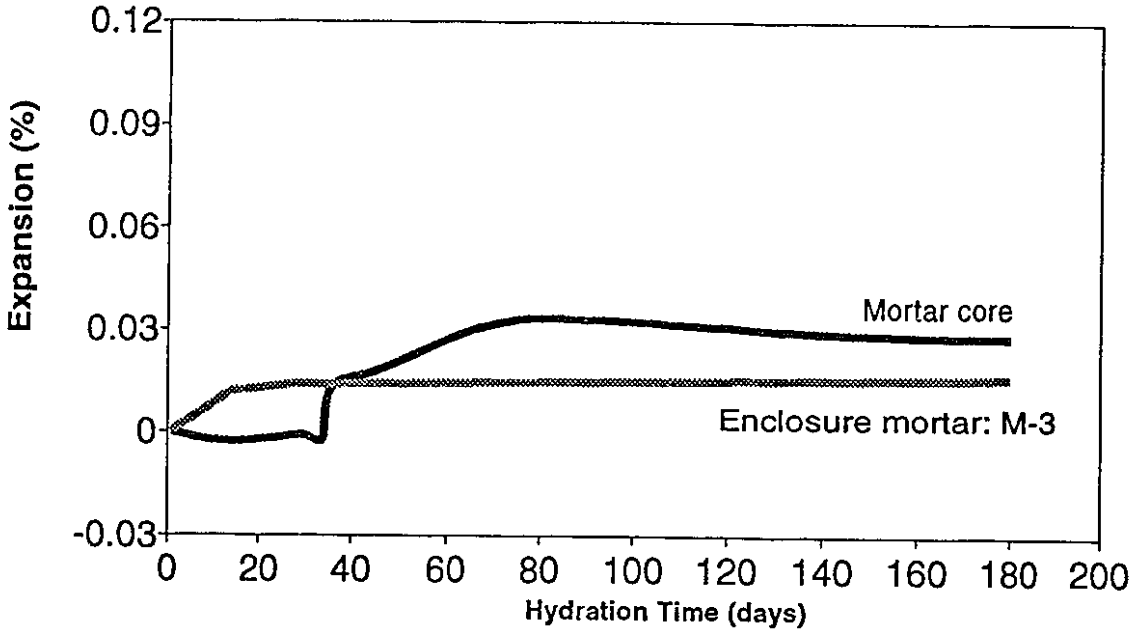
Fig. 5-2. Expansion at the open mouth of a pre-existing crack in Portland cement mortar surrounded by M-1 mortar.



Specimen Designation	Additives (mass % of cement)
Mortar Core	None
M-2	ettringite mixture I* (5%)

* *It was prepared at 85 °C. The stoichiometric amount of reagent aluminium sulphate and calcium hydroxide required for ettringite formation was mixed with sufficient distilled water in a sealed plastic bottle. The mixture was reacted at 85 °C in a water bath for 30 days. The wet mixture was then vacuum dried for 48 hours.*

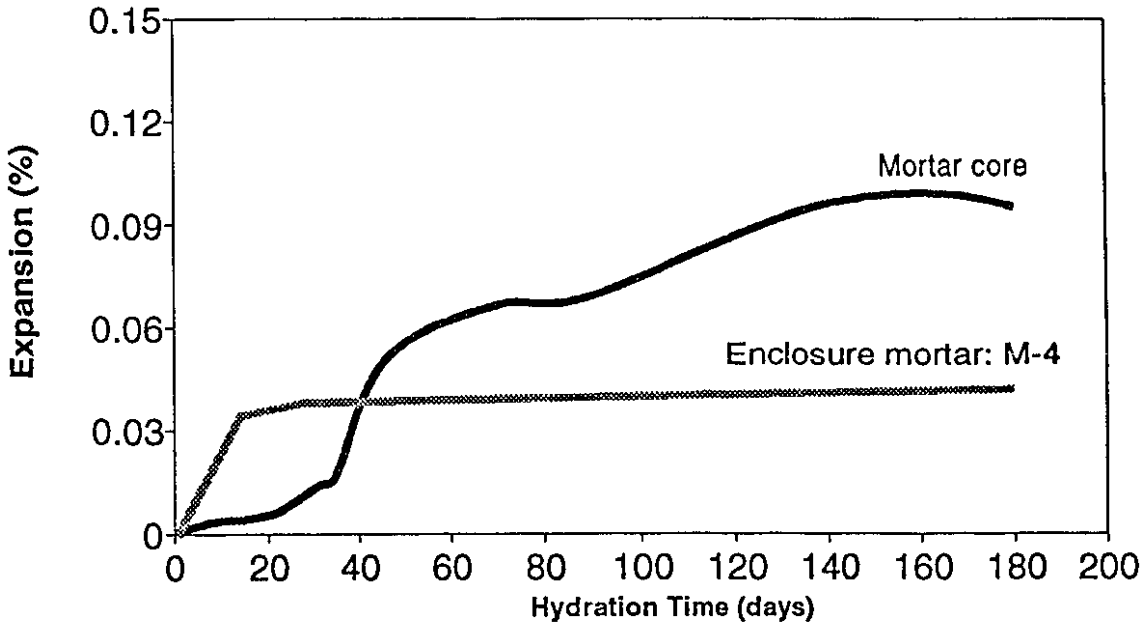
Fig. 5-3. Expansion at the open mouth of a pre-existing crack in Portland cement mortar surrounded by M-2 mortar.



Specimen Designation	Additives (mass % of cement)
Mortar Core	None
M-3	ettringite mixture II* (5%)

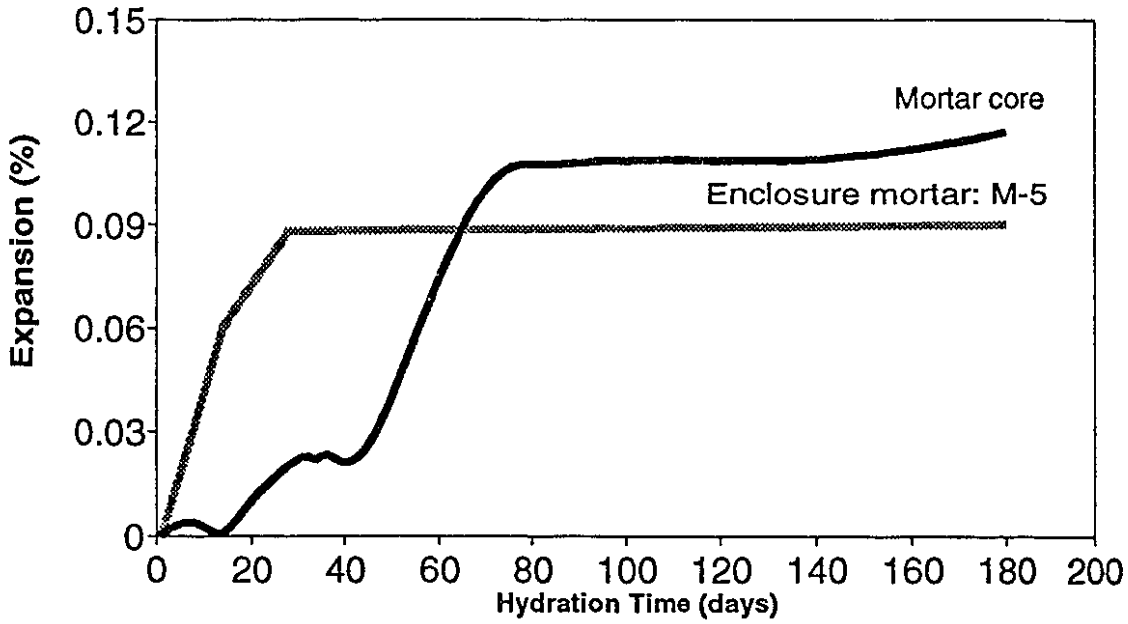
* *It was prepared at 23 °C. The reactants and the preparation procedure were the same as the Ettringite mixture I (see fig. 5-3).*

Fig. 5-4. Expansion at the open mouth of a pre-existing crack in Portland cement mortar surrounded by M-3 mortar.



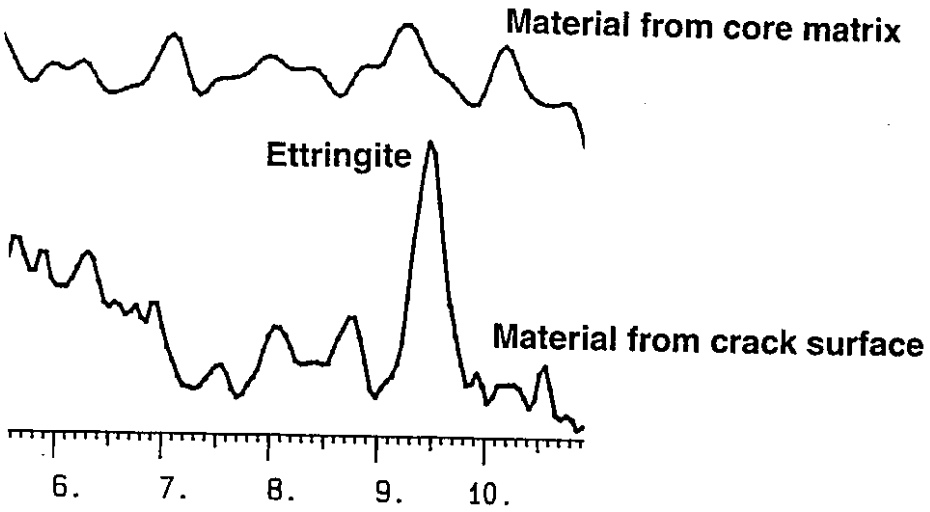
Specimen Designation	Additives (mass % of cement)
Mortar Core	None
M-4	C_3A (10%) + gypsum (5%)

Fig. 5-5. Expansion at the open mouth of a pre-existing crack in Portland cement mortar surrounded by M-4 mortar.

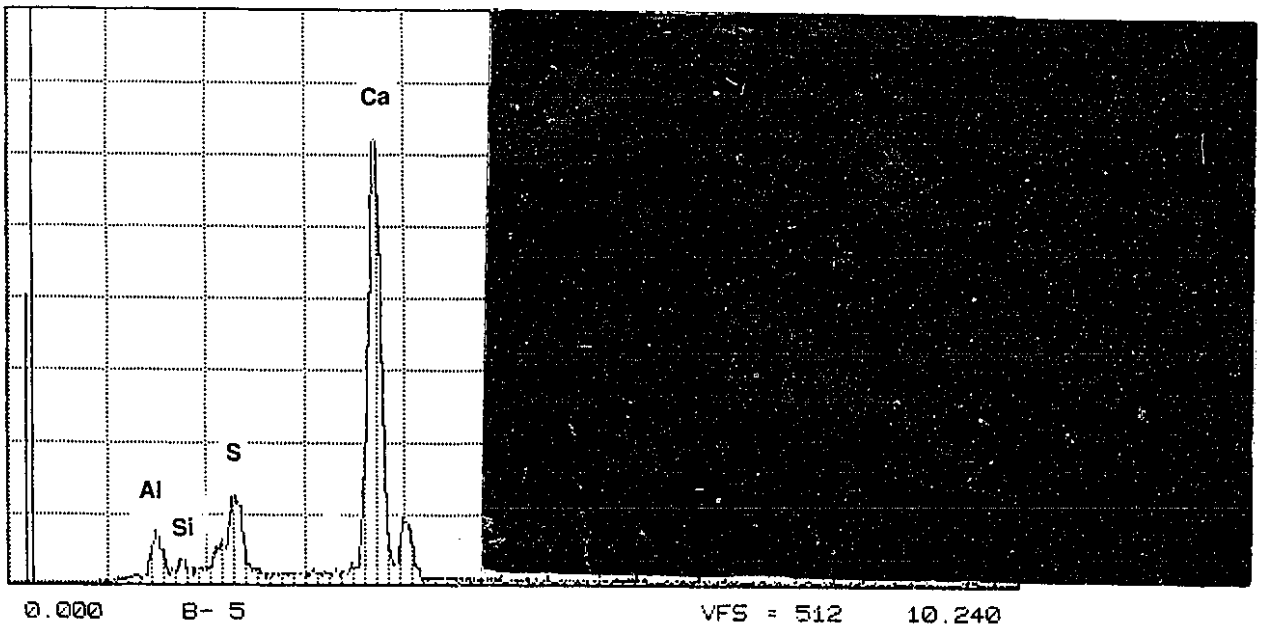


Specimen Designation	Additives (mass % of cement)
Mortar Core	None
M-5	$Al_2(SO_4)_3$ (3%) + $Ca(OH)_2$ (2%)

Fig. 5-6. Expansion at the open mouth of a pre-existing crack in Portland cement mortar surrounded by M-5 mortar.



(a) X-ray diffraction spectrum of the crack surface of Type 50 Portland cement mortar core.



(b) Photomicrograph from the SEM and EDXA investigation of the crack surface of Type 50 Portland cement mortar core.

Fig. 5-7. Ettringite formation on the surface of a pre-existing Crack.

§ 5.4. Discussion

Once an internal sulphate source as described above exists, aluminate and sulphate ions are gradually released. These ions then diffuse into the concrete pore solution to sites suitable for ettringite crystallization. Ettringite preferentially crystallizes in pre-existing cracks which then open, resulting in the expansion of the material. Extension of the crack leads to damage of cement paste. The crystallization rate is dependent on the degree of supersaturation of the reactants required to form ettringite nuclei. These reactants can only come from the enclosure mortar and by diffusion through the ettringite-free cement mortar wall. The concentration of reactants (Al^{3+}, Ca^{2+} and $SO_4^{=}$) in the specimens during the process of ettringite formation might be higher than that in the equilibrium system containing pre-formed ettringite. A high reactant concentration results in a high diffusion rate of reactant ions. This accelerates crystallization and subsequent expansion. It is apparent that ettringite formation in the crack occurs by a through-solution mechanism.

§ 5.5. Conclusions

Stages in the deterioration of concrete due to delayed ettringite formation can be described as follows:

(1) Presence of an internal sulphate source

High adsorption of sulphate by C-S-H gel cured at high temperature and slow desorption of sulphate at later ages are important processes for delayed ettringite formation. The critical temperature for sulphate adsorption by C_3S hydrates appears to be above 65 °C.

(2) Diffusion of reactants into pre-existing cracks through concrete pore solutions

Water curing accelerates delayed ettringite formation by providing a medium for diffusion of reactants, i.e. satisfying the requirements of a through-solution process.

(3) Preferred crystallization of ettringite in cracks

Preferred crystallization of ettringite in cracks results in the extension of cracks and the damage of concrete.

Chapter 6

CRACKING IN CONCRETE DUE TO DELAYED ETTRINGITE FORMATION

- Different Treatments Following High Temperature Curing
- Cracking in Portland Cement Products

§ 6.1. Introduction

Several case studies on high temperature (75-80 °C) moist-cured concrete products have been reported (see § 2.5.). The investigations revealed that ettringite usually was present in cracks, voids and the transition zone at the aggregate-binder interface. Study on the post-cracking behavior of moist-cured concrete (75-80°C) railway sleepers indicated that microcracks were the primary cause of deterioration. The initial cracks resulting in such deterioration might occur during thermal treatment. Highly concentrated ettringite crystals were found in the transition zone. Pre-existing cracks in concrete appear to be an important factor in the deterioration of concrete when internal sulphate sources exist as mentioned above. A rapid method, the so-called the Duggan test, to determine the potential expansion due to delayed ettringite formation was reported by Grabowski et al. (1992). Apparent expansion was found in the concrete samples after treatment involving several severe heat-drying/wetting cycles to simulate certain service conditions such as those experienced by railway sleepers. The accelerated process obviously created microcracks in the tested concrete specimens. This was then believed to be a critical condition to cause DEF.

The objective of the work reported in this chapter is to study the relative potential of different cement types and treatments following moist curing at elevated temperature on microcrack formation and subsequent deterioration of concrete due to DEF.

§ 6.2. Experimental

§ 6.2.1. Materials

Type 10, Type 30 and Type 50 portland cements were used in this study. The fineness values and oxide composition of the cements are shown in Table 1. Minus 25 mm crushed limestone was used as the coarse aggregate, and the fine aggregate was natural river sand. They were all washed using tap-water and dried at room temperature.

The specific gravities of the coarse and fine aggregates were 2.56 and 2.65 respectively. The aggregate was in the saturated-surface-dry state.

Table 6.1. Fineness, Mineralogical and Oxide Compositions of Portland Cements

	Fineness (cm^2/g)	Mineralogical Composition (%)			
		C_2S	C_3S	C_3A	C_4AF
Type 10	2560	21.52	52.88	6.20	8.40
Type 30	5682	16.07	54.21	10.26	5.81
Type 50	4198	15.35	58.67	2.77	13.33

	Oxide Composition (mass %)							
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O +K_2O	SO_3	L.I.
Type 10	21.42	4.10	62.43	2.76	3.73	.53	2.45	2.03
Type 30	19.87	5.09	62.34	1.91	2.98	0.60	4.08	2.48
Type 50	20.79	3.84	62.78	4.38	3.37	0.81	2.40	0.89

§ 6.2.2. Specimen Preparation

§ 6.2.2.1. Concrete

Concrete having a water/cement ratio = 0.43 and a cement:sand:stone ratio of 1.00:1.14:2.32 by mass was prepared. The fresh concrete containing Type 10, Type 30 or Type 50 portland cement was mixed for 5 minutes and then cast in PVC molds, 200 mm long by 100 mm in diameter. The concrete cylinders were kept at room temperature for one hour. They were then put in a sealed curing-box at 100% relative humidity and placed in an oven. The temperature of the specimen reached 85 °C after one hour heating. The concrete specimens were moist-cured at 85 °C for 12 hours and then cooled naturally to room temperature. Different treatments to create microcracks were applied after 24 hours (Table 6.2):

Table 6.2. Treatments Applied to the Concrete.

Treatment	Description
Control	Continuously cured in lime-water at 23 °C, as a reference specimen.
85 °C drying/re-wetting	85 °C drying in the oven for 24 hours and then cooling to ambient temperature; re-wetting at 23 °C.
23 °C drying/re-wetting	Drying at 23 °C and 50% R.H. for 14 days; re-wetting at 23 °C.
Loading/unloading	10 loading/unloading cycles followed by drying under ambient condition for 14 days. Loading to 90% of compressive strength was applied; each increment of load was held for 3 minutes.
Freezing/thawing	14 freezing and thawing cycles. A cycle consisted of 12 hours freezing at -24 °C and 8 hours thawing in water at ambient temperature.

The specimens were placed in lime-water after the microcrack-inducing treatments. The specimens were cured in lime-water for at least 14 days to allow the length recovery to a stable value. Studs were installed at the ends of the specimen to facilitate measurement of the longitudinal expansion. Two studs were installed on the side of the cylinder for the measurement of lateral expansion. The initial length and diameter of the cylinders were measured on the concretes after the 14 days in lime - water. The expansion of the concrete specimens was recorded at designated times following the initial measurement.

§ 6.2.2.2. Type 30 Portland Cement Mortar

Preliminary attempts to develop a test method to evaluate the DEF potential of given cements were carried out on an Type 30 cement mortar specimen. The prism specimen had dimensions of 77x77x298 mm. Natural river sand was used. The sand to cement mass ratio was 2.75 and the water to cement ratio was 0.4. The fresh mortar was mixed for 3 minutes and then cast into steel molds. The curing procedures of the mortar specimens were the same as those of concrete specimens. The temperature of the specimens reached 95 °C after one hour heating. After cooling, hardened mortar specimens were dried at 85 °C for 24 hours and then placed in lime-water at 23 °C. Control specimens with the same composition but moist-cured at 23 °C were also prepared. The initial length of the cooled specimens was measured immediately after the

initial curing (e.g. high-temperature curing). Expansion was recorded every week. Photographs of the crack patterns were taken and crack density values calculated. The samples were then intentionally fractured along the crack and beyond. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) were performed on the cracked surfaces. X-ray diffraction (XRD) analysis was carried out on the cement paste. Cement paste was prepared by carefully grinding and sieving the mortar sample. A Cambridge Stereoscan S250 SEM/EDXA instrument and a Rigaku X-ray Diffractometer System D/Max -B with copper Kα radiation were used.

§ 6.3. Results

§ 6.3.1. Concrete

The longitudinal and lateral expansion of concrete specimens with hydration time are shown in Figs. 6-1 to 6-10. The test confirmed that only a high temperature cured Type 30 cement concrete followed by severe heat-drying suffered large expansion due to delayed ettringite formation (DEF). The other treatments, such as loading/unloading cycles, freezing/thawing cycles and room temperature drying, appeared not to cause significant DEF-induced expansion. However some swelling was found in all the specimens. It is believed that less than 0.1% swelling occurs normally when cement is cured in lime-water and will not cause any durability problem to the concrete. The lateral swelling of the concrete cylinders appeared to be relatively larger than the longitudinal swelling. This was particularly true for the concrete made with Type 30 cement. The reason is not clear and is the subject of ongoing investigation. However this is not germane to the central argument. The longitudinal expansion of heat-dried Type 30 cement concrete increased to about 0.2% after 110 days curing and reached about 0.5% at 250 days. The lateral expansion of this concrete, which reached 0.2% at 75 days,

developed earlier than the longitudinal expansion. The 250-day lateral expansion value was less than the longitudinal expansion.

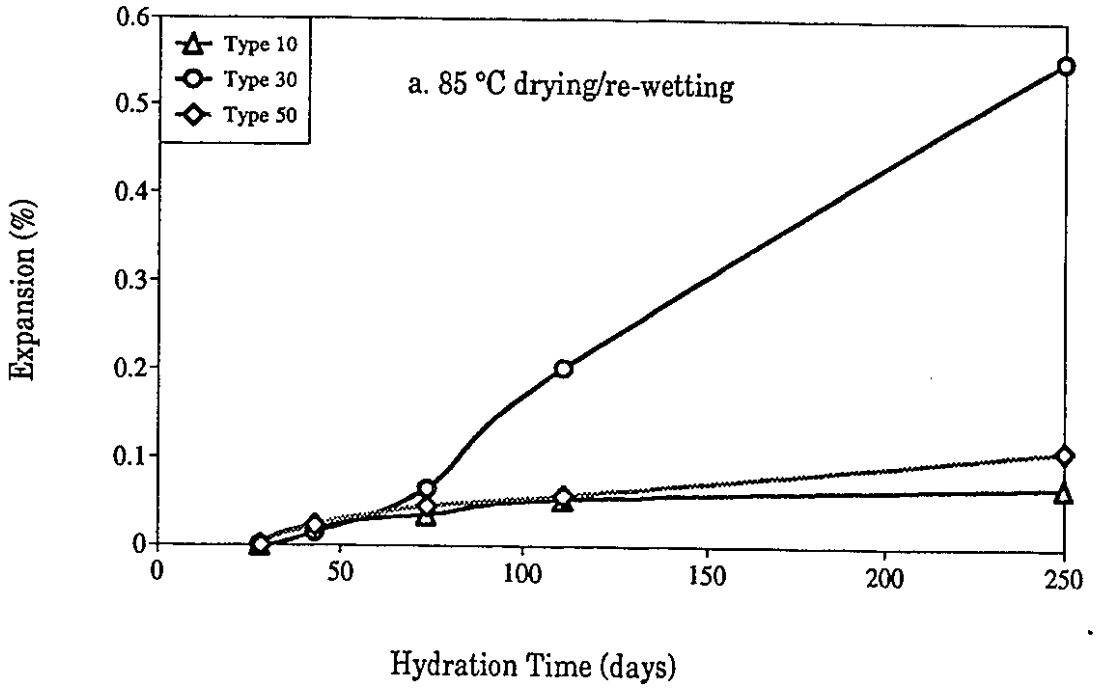


Fig. 6-1. Longitudinal expansion of the concrete subjected to 85 °C drying/re-wetting treatment (See Table 6.2).

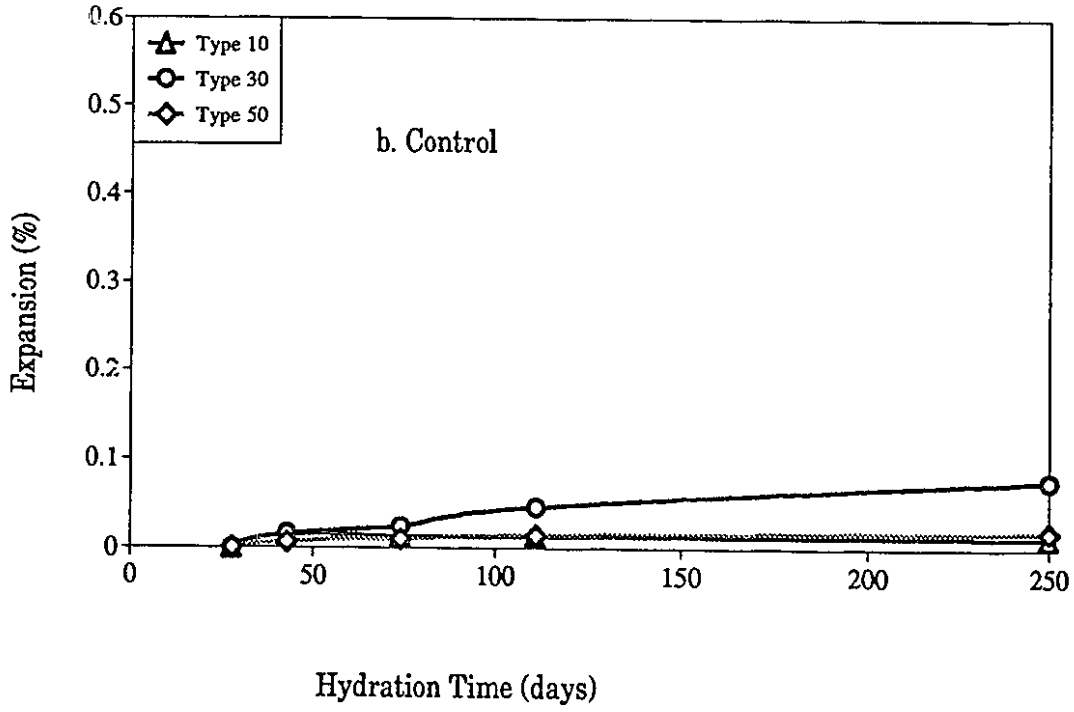


Fig. 6-2.Longitudinal expansion of the control concrete treatment (See Table 6.2).

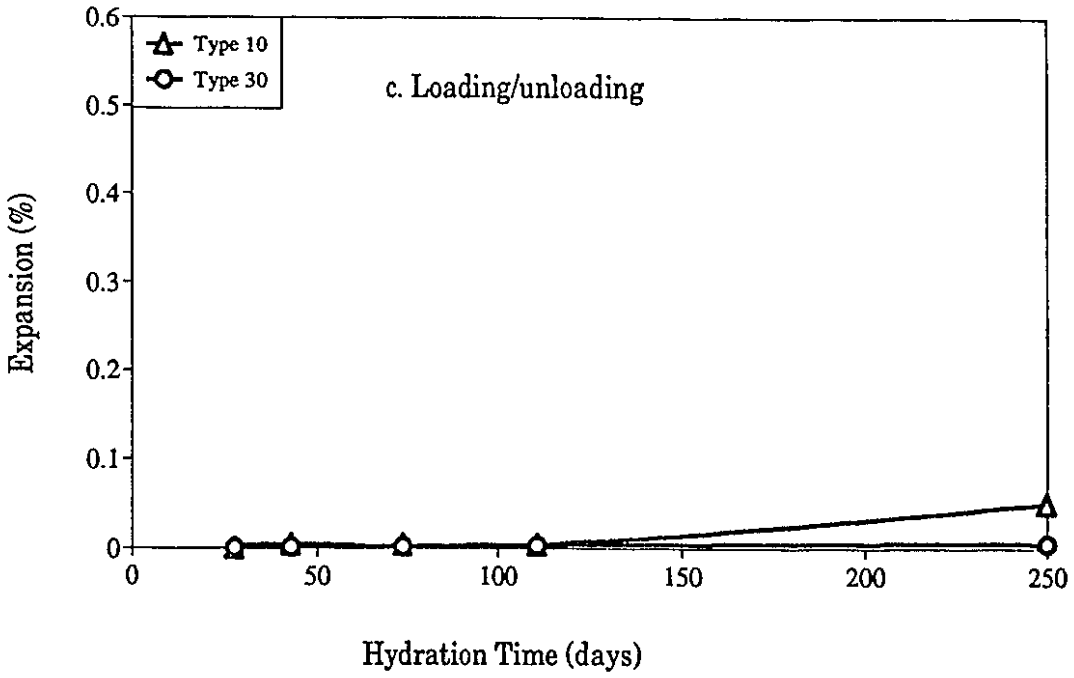


Fig. 6-3.Longitudinal expansion of the concrete subjected to loading/unloading treatment (See Table 6.2).

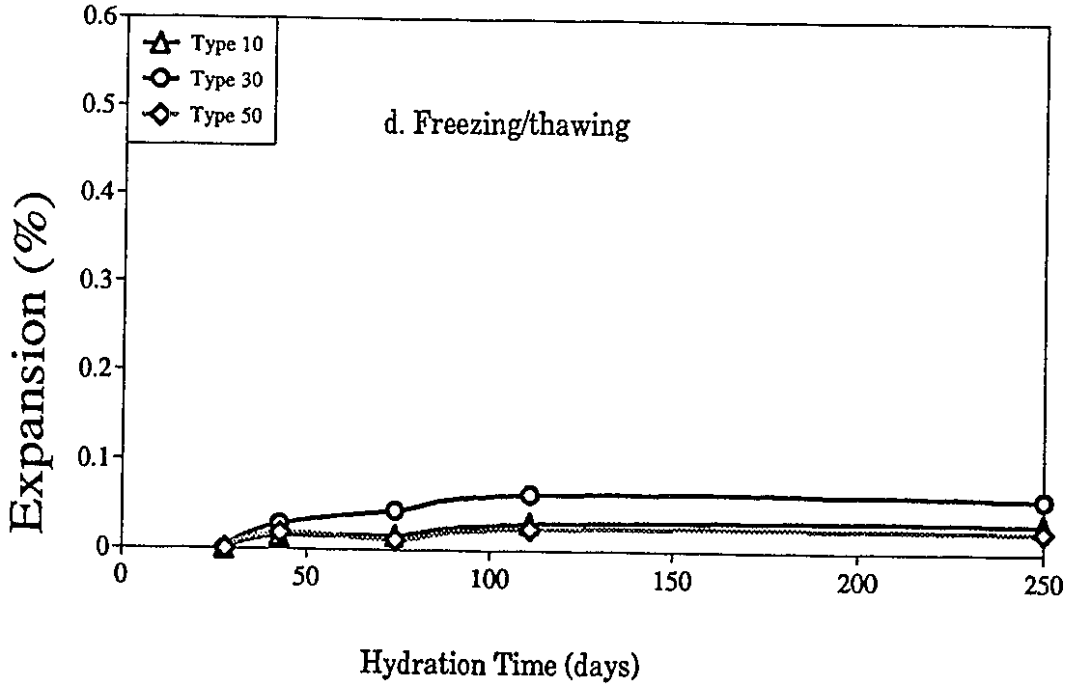


Fig. 6-4.Longitudinal expansion of the concrete subjected to Freezing/thawing treatment (See Table 6.2).

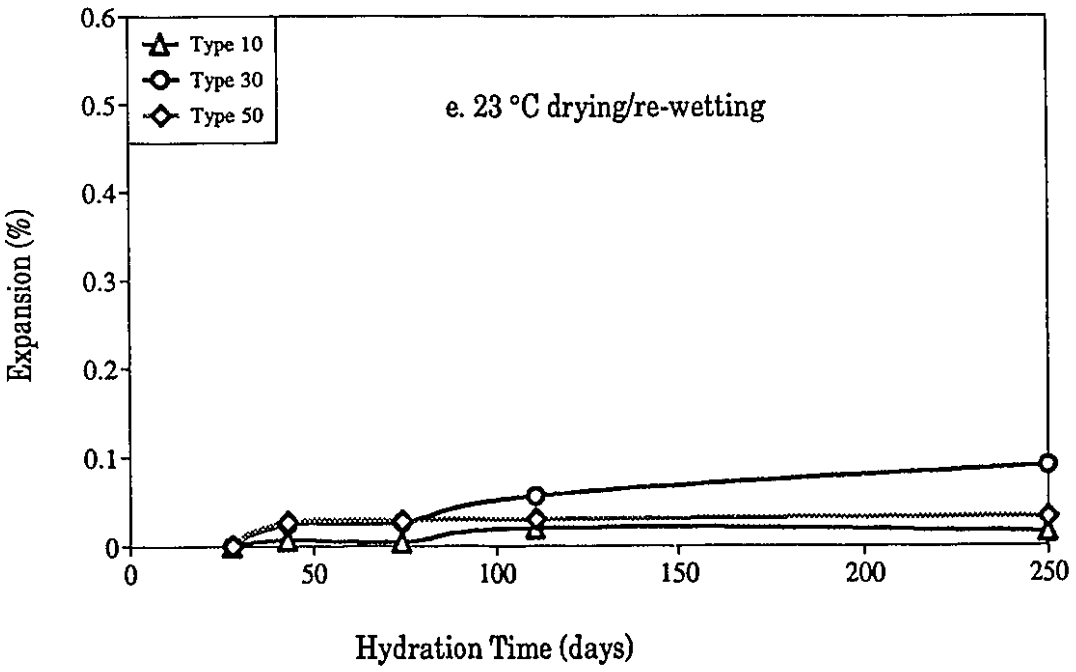


Fig. 6-5. Longitudinal expansion of the concrete subjected to 23 °C drying/re-wetting treatment (See Table 6.2).

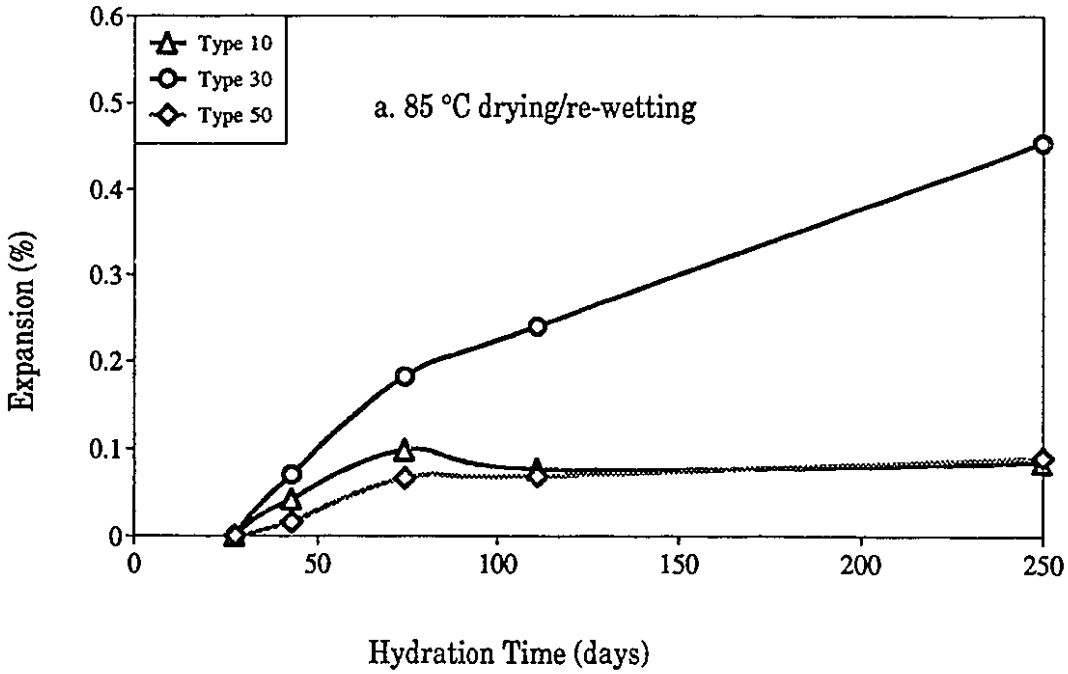


Fig. 6-6. Lateral expansion of the concrete subjected to 85 °C drying/re-wetting treatment (See Table 6.2).

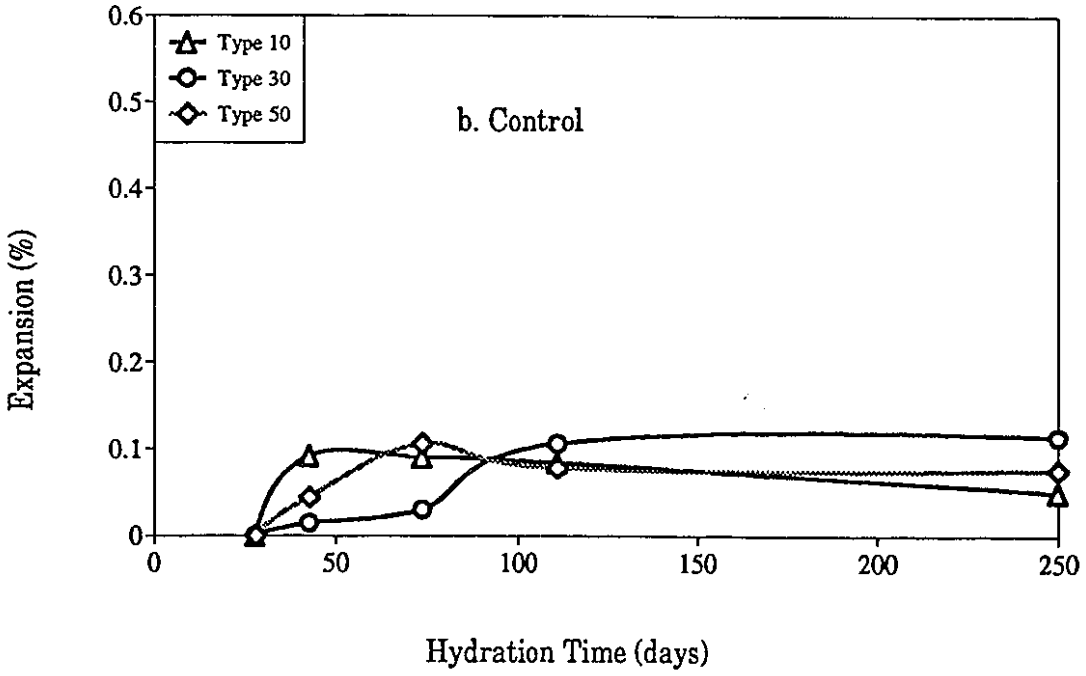


Fig. 6-7.Lateral expansion of the control concrete treatment (See Table 6.2).

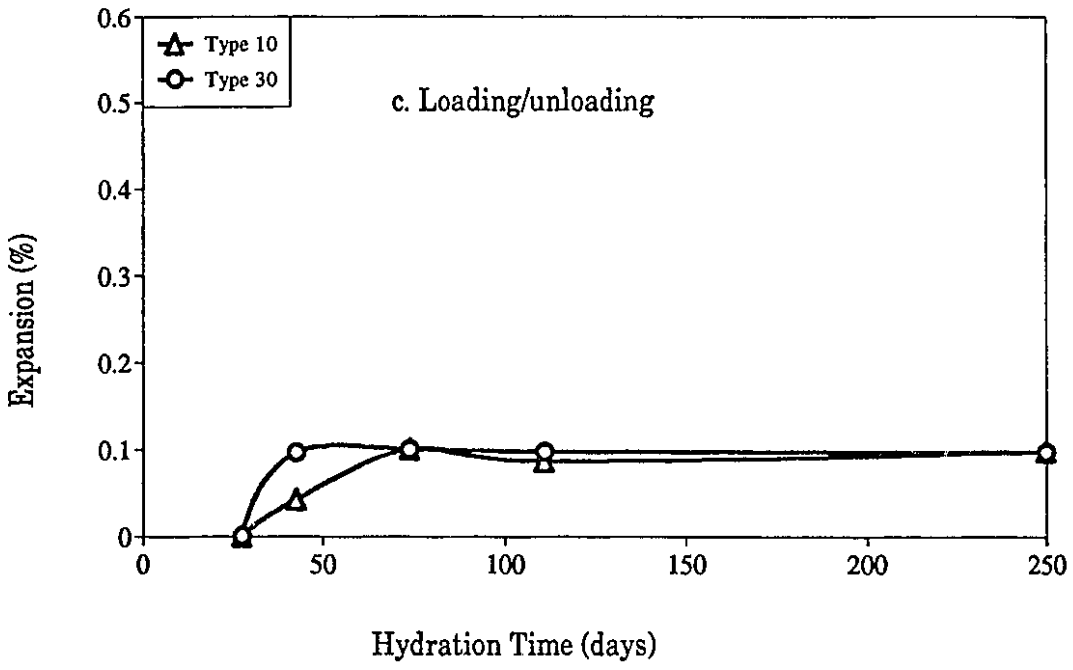


Fig. 6-8.Lateral expansion of the concrete subjected to loading/unloading treatment (See Table 6.2).

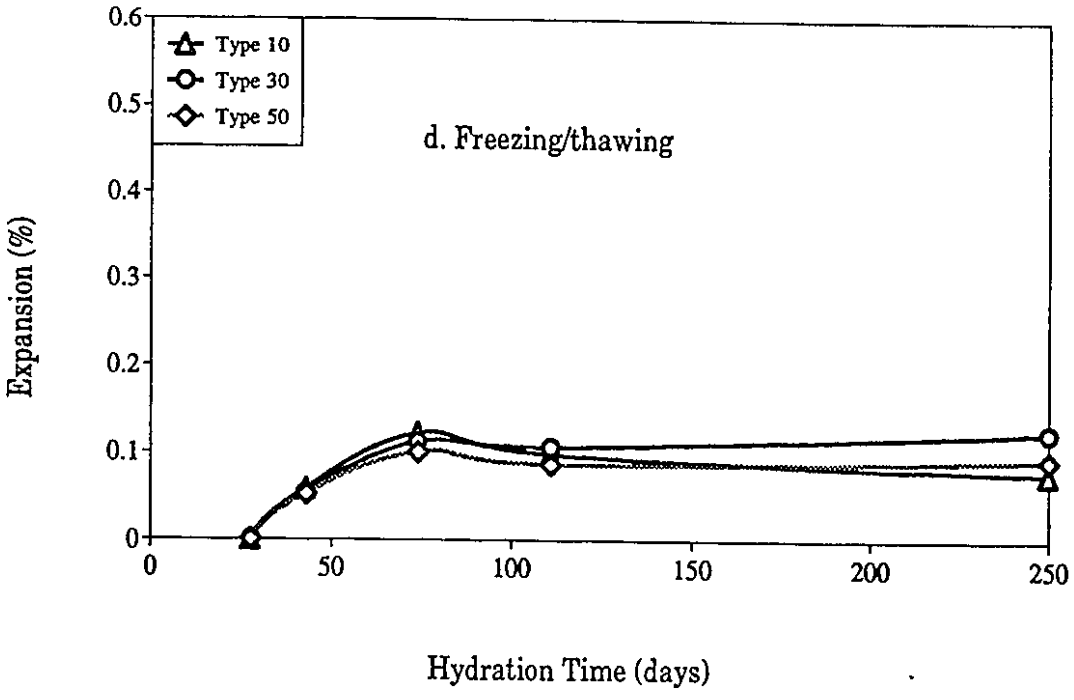


Fig. 6-9.Lateral expansion of the concrete subjected to Freezing/thawing treatment (See Table 6.2).

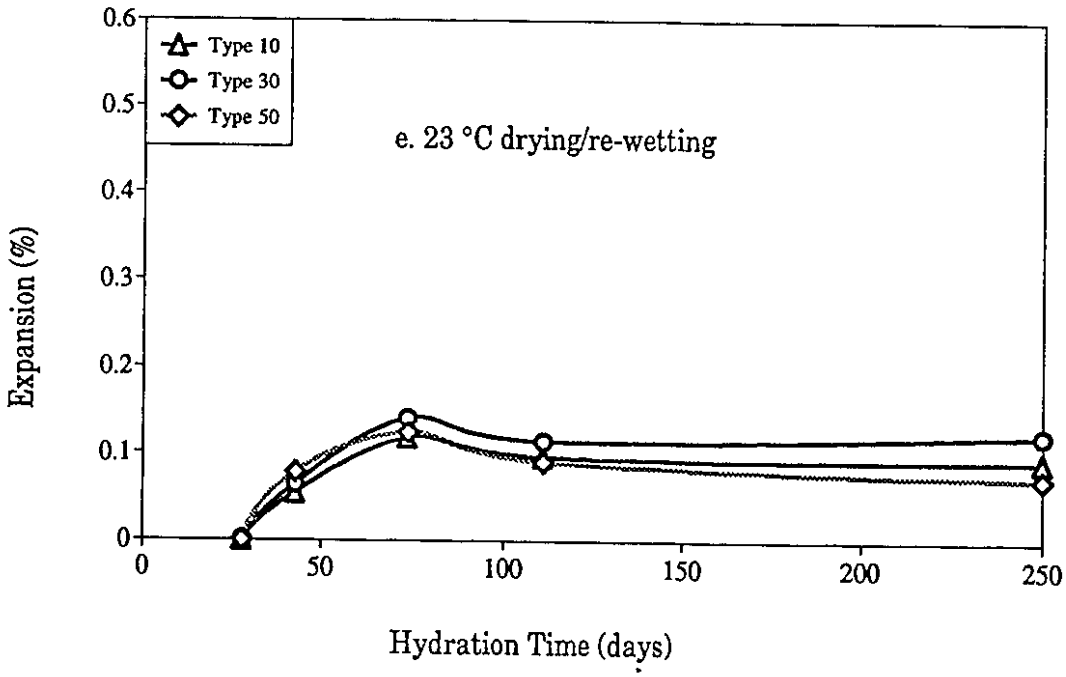


Fig. 6-10. Lateral expansion of the concrete subjected to 23 °C drying/re-wetting treatment (See Table 6.2).

§ 6.3.2. Cement Mortar

The effect of curing conditions and subsequent treatment on Type 30 portland cement mortar is shown in Fig. 6-11. The control mortar, moist-cured at room temperature, did not show expansion; the specimen, moist-cured at 95 °C and followed by thermal-drying, started to expand at about 40 days. The expansion accelerated at 60 days and reached a maximum at about 160 days. The ultimate expansion value was about 1.0%. The expansion of cement mortar was apparently larger than that of the concrete. This may be due to (1) the higher initial curing temperature (95 °C) for the mortar than the concrete specimen (85 °C); (2) more Type 30 cement contained in a unit volume of mortar specimen than in the concrete.

Visible cracks were found on the surface of the expanded specimen at about 90 days. The cracks extended with time. A photograph of the crack pattern was taken at 180 days (Fig. 6-12). The crack density on the surface of the specimen was 36.2 m/m^2. The XRD analysis was carried out on cement pastes taken from the mortars (Fig. 6-13). An intense peak of ettringite at d-spacing=0.97 nm (9.2°, 2θ) was recorded for the expanded mortar. It was not detected in the mortar sample cured only at room temperature. The investigation on the cracked surfaces was performed using SEM/EDXA analysis (Fig. 6-14). The entire area of the crack surfaces was covered with ettringite crystals (Fig. 6-14a). The size of the ettringite crystals was typically about 1-2 μm long and 0.3 μm in diameter. The EDXA spectrum showed that the crystals contained mainly calcium, sulfur and aluminum. The sulfur peak was much higher than that usually found in normal Portland cement paste, indicating that sulphate ions had migrated from the cement matrix into the cracks to satisfy the supersaturation condition for ettringite crystallization.

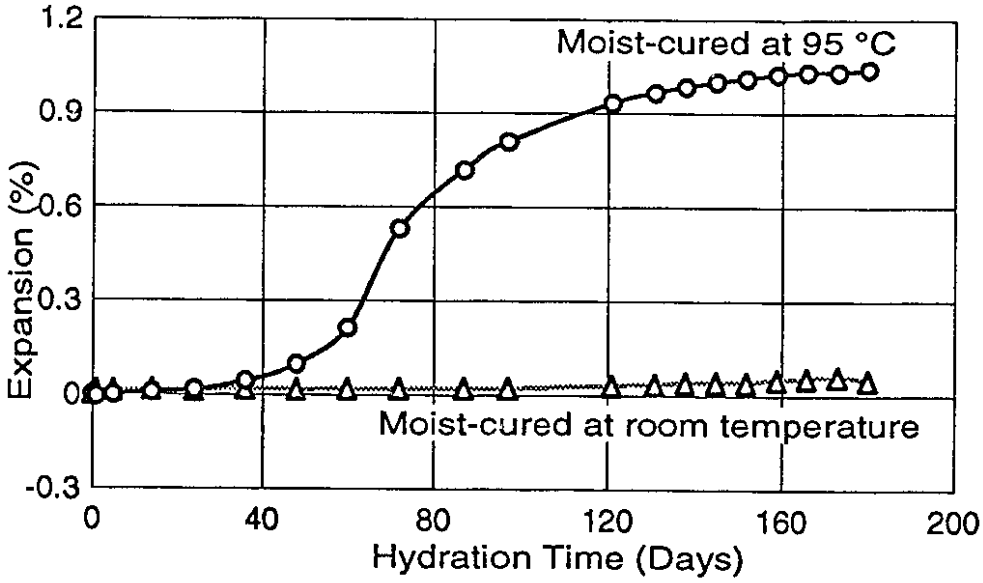


Fig. 6-11. Expansion of Type 30 cement mortars.

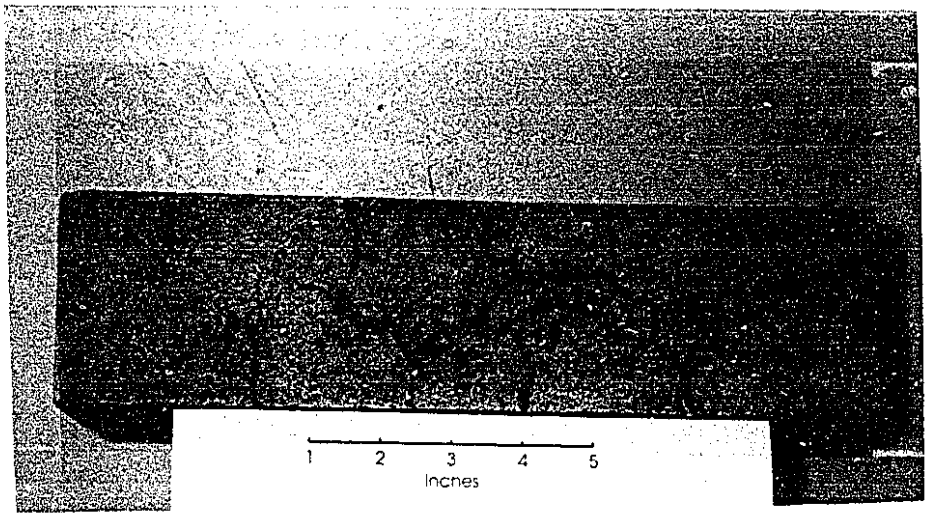


Fig. 6-12. Cracking of Type 30 cement mortar (initially cured at 95 °C) followed by 85 °C drying, after 180-days) curing in lime-water 23 °C.

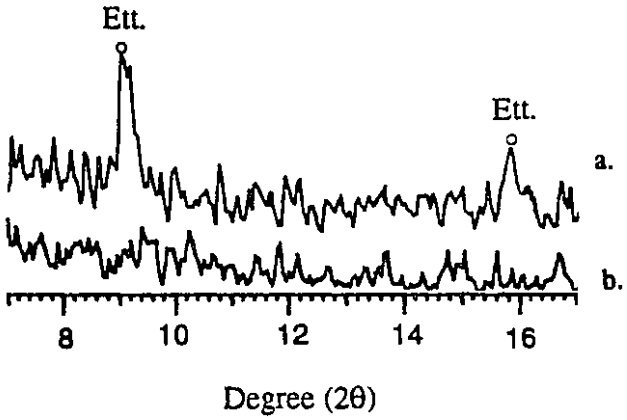


Fig. 6-13. XRD spectra of Type 30 cement pastes. (a) moist-cured at 95 °C followed by 85 °C drying; (b) moist-cured at 23 °C.

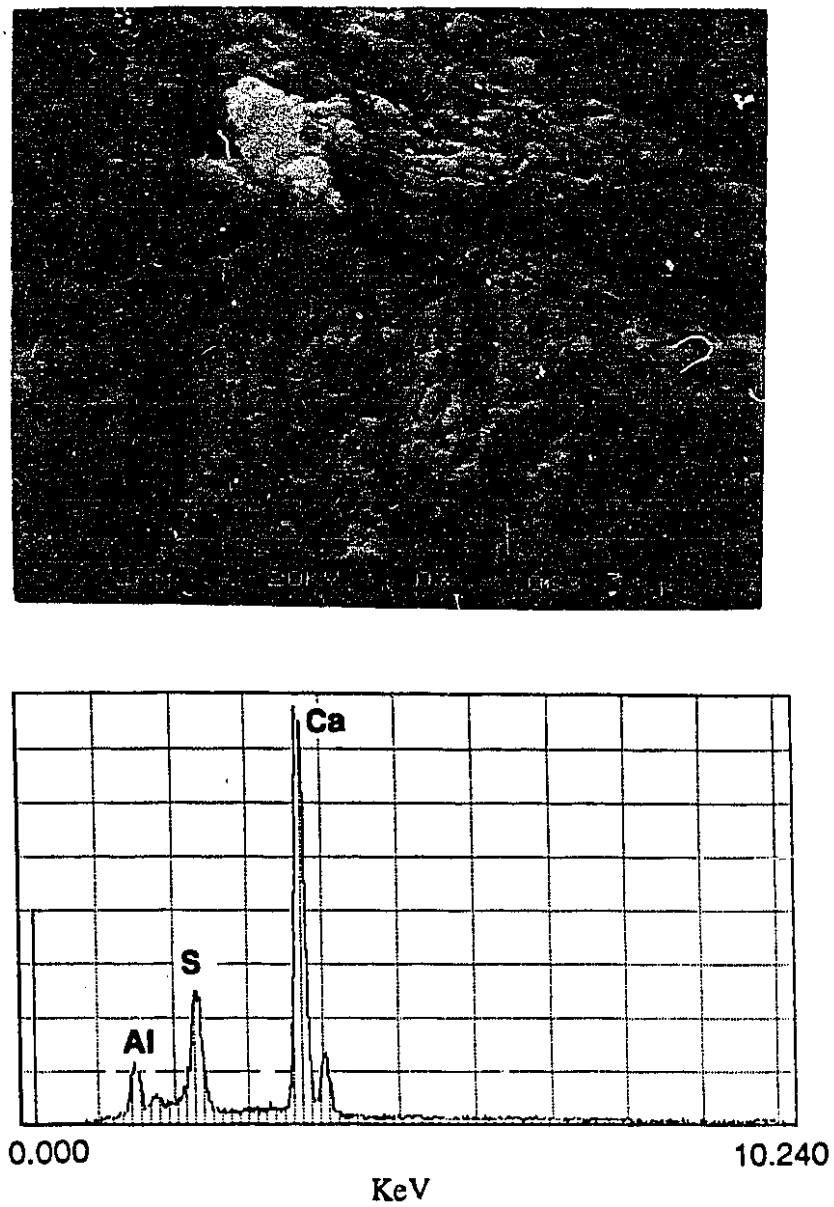


Fig. 6-14. SEM/EDXA analysis on a crack surface of Type 30 cement mortar (initially cured at 95 °C followed by 85 °C drying) after 180-day curing in lime-water at 23 °C.

§ 6.4. Discussion

Three parameters appear to influence expansion behavior due to DEF:

- Cement type, e.g. high blaine fineness and SO_3 content;
- High temperature moist-curing;
- Severe thermal-drying.

It is well-known that Type 30 Portland cement may contain more C_3A and SO_3 in the form of calcium sulphate than Type 10 cements. Gypsum is normally used in portland cement to regulate its setting behavior. The Type 30 portland cement contains more C_3A in order to promote high early strength. The Type 30 cement can contain SO_3 of higher than 4.0%. The maximum SO_3 content in the Type 10 or Type 50 cement is, however, generally less than 3.5%. The Type 30 cement is much finer than the other types. Type 30 cement with fineness of higher than 5000 cm^2/g is normally produced. High temperature curing makes it possible for Type 30 cement to hydrate and form more C-S-H gel quickly during the heat-curing period. Previous studies (Chapter 3) indicate that C-S-H gel can adsorb sulphate rapidly at temperatures higher than 65 °C. These sulphate ions are released more slowly at later ages. This is the so-called internal sulphate source. Therefore, high curing temperature and quick formation of C-S-H gel from finely-ground cement are the major factors controlling the internal sulphate source. A high SO_3 content in the cement increases the amount of sulphate stored in the internal sulphate source available for DEF. Rapid formation of C-S-H gel from Type 30 cement also increases the density of the microcracks formed at early ages due to drying shrinkage. Thermal-drying enhances the creation of microcracks. The measured expansion is a macro phenomenon resulting from the cumulative effect of microcrack formation. Drying of a C-S-H rich concrete at 85 °C may be more severe (more conducive to microcrack formation) than the other treatments, e.g. 10 loading/unloading cycles, 14 freezing/thawing cycles or

room temperature drying. These microcracks exist in the cement matrix and especially in the transition zone between aggregates and cement paste. The cracks in the concrete subjected to loading and unloading or freezing and thawing cycles usually occur in certain weak areas. Therefore the crack density (at least in these tests) appears to be less than that in the thermal-dried Type 30 cement concrete. Expansion is a direct result of crack opening processes. Ettringite is believed to preferentially nucleate and grow in pre-existing cracks. The sulphate ions released from the internal source, i.e. the C-S-H complex or Kalousek's "phase X", will likely migrate to the nearest crack. Nucleation of ettringite crystals occurs, if the concentration of aluminate in the crack is sufficient to create supersaturation conditions necessary for forming ettringite. Calcium aluminate is present primarily in the solid state. The solubility of the aluminate hydrates is relatively low, and thus aluminate ions do not migrate as readily as sulphate ions. Therefore, mobilization of sulphate in the concrete determines the rate of DEF and hence the expansion. Ettringite formation in large voids may not cause the deterioration of the concrete. Growth in cracks will easily extend the cracks and requires much less energy than creating a new crack in the concrete.

Damage of concrete due to DEF has been reported primarily in concrete members subjected to moist curing followed by open-air weathering and hence drying/re-wetting cycles, e.g. precast front panels and railway sleepers [Heinz and Ludwig (1986)]. Cases have been observed in Germany [Sylla (1988); Neck (1988)], Finland [Tepponon and Erickson (1987)], Australia [Shayan and Quick (1992)], South Africa [Oberholster (1992)], Canada [Duggan and Scott (1988)] and USA [Marusin (1995)]. These concretes were mostly made with high early strength portland cement and accelerated moist curing was employed. The products underwent drying/wetting, freezing/thawing and fatigue cycles year around. Heat-drying is experienced during summer. These microcrack-

inducing processes and hence DEF are always found in moist cured out-door concrete structures.

§ 6.5. Conclusions

1. Concrete made with Portland cement having high Blaine fineness and SO_3 content is vulnerable to the deterioration due to delayed ettringite formation (DEF).

2. High temperature curing followed by severe thermal-drying promotes concrete deterioration due to DEF.

3. Cracking occurs in mortar, made with Type 30 Portland cement and subjected to high temperature curing followed by severe thermal-drying, at about 90 days. The crack surfaces are covered with ettringite crystals.

Chapter 7

A PROPOSED TEST METHOD TO DETERMINE THE POTENTIAL FOR DELAYED ETTRINGITE FORMATION IN A PORTLAND CEMENT

- Test Conditions and Procedures
- Expansion/Time Criteria
- Differences Between the Duggan Test and the Proposed Test Method
- "Delayed Ettringite Formation" and "Secondary Ettringite Formation"

§ 7.1. Introduction

Deleterious expansion of Portland cement products due to delayed ettringite formation has been reported from many countries (See § 2.5.). There is however general agreement on some key conditions that are required for the occurrence of DEF. These conditions are particularly relevant to the precast concrete industry in mitigating long-term damage. Three criteria for optimizing DEF were suggested as follows:

(1) portland cement with a high SO_3/Al_2O_3 ratio and high alkali content;

(2) high curing temperatures;

(3) exposure to a moist environment.

A rapid test (referred to as the Duggan test) to determine the potential expansion due to secondary ettringite formation (SEF) was reported by Grabowski et al [16]. Significant expansion was found in the concrete samples after several severe heat-drying/re-wetting cycles used to simulate certain service conditions relevant to the performance of railway sleepers.

The objective of this study was to develop a test method to determine the DEF potential of a given portland cement. The evaluation criteria in terms of expansion limits and differences between the Duggan test and this proposed test method are discussed.

§ 7.2. Experimental

§ 7.2.1. Materials

Portland Cements: Seven portland cements were used. Their oxide composition and fineness values are listed in Table 7.1.

Natural River Sand: The grading curve of the natural river sand used in this study is shown in Table 7.2.

Coarse River Sand: The coarse river sand used was separated from the natural river sand (3.33-0.85 mm).

Fine River Sand: The fine river sand used was separated from the natural river sand (less than 0.85 mm).

Graded Standard Sand: This material conformed to the requirements for graded standard sand in ASTM Specification C 778.

20-30 Standard Sand: This material conformed to the requirements for graded standard sand in ASTM Specification C 778.

Table 7.1. Fineness, Mineralogical and Oxide Compositions of Portland Cements

Cement	Fineness (cm^2/g)	Mineralogical Composition (%)			
		C_2S	C_3S	C_3A	C_4AF
Type 10-1	3729	21.52	52.88	6.20	8.40
Type 10-2	3611	19.25	53.54	9.87	6.51
Type 10-3	3335	12.02	60.49	5.69	9.92
Type 10-4	3407	20.21	56.25	8.42	5.96
Type 30-1	5682	16.07	54.21	10.26	5.81
Type 30-2	5147	15.33	60.25	7.58	5.48
Type 50	4198	15.35	58.67	2.77	13.33

Cement	Oxide Composition (mass %)							
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O +K_2O	SO_3	L.I.
Type 10-1	21.42	4.10	62.43	2.76	3.73	.53	2.45	2.03
Type 10-2	20.80	5.09	63.20	2.14	2.48	1.12	2.95	1.26
Type 10-3	20.11	4.23	62.58	3.26	2.37	0.85	2.93	2.93
Type 10-4	21.85	4.43	63.91	1.96	3.70	0.81	1.86	0.81
Type 30-1	19.87	5.09	62.34	1.91	2.98	0.60	4.08	2.48
Type 30-2	21.20	4.01	64.05	1.80	2.68	0.69	3.46	1.53
Type 50	20.79	3.84	62.78	4.38	3.37	0.81	2.40	0.89

Table 7.2. Grading of Sand

Sieve	Percentage Passing				
	River	River-f	River-c	Graded	20-30
4.75-mm (No.4)	100	-	-	-	-
3.33-mm (No.6)	93	-	100	-	-
1.18-mm (No.16)	81	-	62	100	100
850-µm (No.20)	73	100	30	-	85 - 100
600-µm (No.30)	60	45	-	98	0 - 5

§ 7.1.3. Mix Design

Mix proportions of the cement mortar mixes used in this study are listed in Table 7.3.

Table 7.3. Mix Proportions of Cement Mortars

Mortar	Mix (mass unit)					Curing Temp. (°C)	Drying Cycles	Results
	Cement		Sand		Water			
	type	content	type	content				No. of Fig.
Type 10-1	Type 10-1	1	river[1]	2.75	0.48	90	1	1, 2
Type 10-2	Type 10-2	1	river	2.75	0.48	90	1	1, 2
Type 10-3	Type 10-3	1	river	2.75	0.48	90	1	1, 2
Type 10-4	Type 10-4	1	river	2.75	0.48	90	1	1, 2
Type 30-1	Type 30-1	1	river	2.75	0.48	90	1	1, 2
Type 30-2	Type 30-2	1	river	2.75	0.48	90	1	1, 2
Type 50	Type 50	1	river	2.75	0.48	90	1	1, 2
90°C curing	Type 30-1	1	river	2.75	0.48	90	1	3, 4
80°C curing	Type 30-1	1	river	2.75	0.48	80	1	3, 4
Graded	Type 30-1	1	graded[2]	2.75	0.48	90	1	5, 6
20-30	Type 30-1	1	20-30[3]	2.75	0.48	90	1	5, 6
river-f	Type 30-1	1	river-f[4]	2.75	0.48	90	1	5, 6
river-c	Type 30-1	1	river-c[5]	2.75	0.48	90	1	5, 6
river	Type 30-1	1	river	2.75	0.48	90	1	5, 6
s/c=1.00	Type 30-1	1	river	1.00	0.48	90	1	7, 8
s/c=2.00	Type 30-1	1	river	2.00	0.48	90	1	7, 8
s/c=2.75	Type 30-1	1	river	2.75	0.48	90	1	7, 8
s/c=3.00	Type 30-1	1	river	3.00	0.48	90	1	7, 8
D3x3x11 1/4	Type 30-1	1	river	2.75	0.48	80	1	9, 10
D1x1x6	Type 30-1	1	river	2.75	0.48	80	1	9, 10
No cycle/III	Type 30-1	1	river	2.75	0.48	80	0	11, 13
1 cycle/III	Type 30-1	1	river	2.75	0.48	80	1	11, 13
3 cycles/III	Type 30-1	1	river	2.75	0.48	80	3	11, 13
5 cycles/III	Type 30-1	1	river	2.75	0.48	80	5	11, 13
No cycle/I	Type 10-1	1	river	2.75	0.48	80	0	12, 14
1 cycle/I	Type 10-1	1	river	2.75	0.48	80	1	12, 14
3 cycles/I	Type 10-1	1	river	2.75	0.48	80	3	12, 14
5 cycles/I	Type 10-1	1	river	2.75	0.48	80	5	12, 14

Note: 1, 2, 3, 4, and 5 are different sands, see Table 7.2.

§ 7.2.3. Specimen Preparation

The mortars were mixed according to the procedure described in ASTM Method C 305. Two 25x25x160-mm test specimens for each cement were prepared. The

temperature of the preparation room, dry materials, and mixing water was maintained at 23 °C. The relative humidity was about 50%.

The specimens were then placed in the moist curing room. All test specimens in the molds were kept in the moist room for 1 hour with upper surfaces exposed to the moist air but protected from dripping water. The specimens were put in a plastic container after pre-storage. The container with the test specimens was tightly covered and sealed. The container was then placed in an oven. The temperature in the container was raised to the designated temperature (e.g. 80 or 90°C) in 60 min and maintained for 12 hours. The heating unit was turned off at 12 hours and the test specimens were cooled for 4 hours by opening the oven door. The specimens were removed from the molds, properly identified, and placed in water maintained at 23°C for 6 hours prior to making the initial length measurement. The specimens were (after the initial length measurement) dried in an oven maintained at 85°C for 24 hours, and subsequently cooled to room temperature. The specimens were then stored in saturated lime water in a tank in the moist room at 23°C.

§ 7.2.4. Length Measurement

The specimens were removed from water storage, and wiped with a damp cloth before measuring. The length change of the specimens was measured using an electronic length comparator.

The first reading on the test specimens was made after 24h from the time the cement and water were mixed together. The subsequent measurements were carried out every 7 days. The average expansion value of the two specimens was used.

§ 7.2.5. Expansion Limits

An expansion limit of 0.04% has been used as a criterion in many ASTM specifications and test methods to evaluate the expansion potential of a portland cement.

Expansion values at 28, 42 and 56 days were determined to facilitate selection of a proper criterion. An expansion value larger than 0.04% was considered to be a failure.

§ 7.3. Results

§. 7.3.1. Effect of Cement Type

The development of expansion of the mortars made with different types of portland cement initially cured at 90 °C is shown in Fig. 7-1. The data presented are for a period of 1 to 90 days. Only three cement mortars (containing Type 30 cements) exhibited deleterious expansion. The Type 30-1 cement presented the highest expansion, beginning after 14 days. Its 90-day expansion value was 1.38%. The expansion of the Type 30-2 cement mortar developed more slowly (after 21 days) than that of Type 30-1 cement mortar. Its 90 day expansion value was still very high (about 0.92%). One Type 10 cement (Type 10-3) mortar showed slightly expansive potential. Its expansion value was much lower than that of the Type 30 cement mortars.

The expansion value of the cement mortars at 28, 42 and 56 days are shown in Fig. 7-2. Only Type 30-1 cement mortar had expansion values greater than the 0.04%-limit at 28 days. Expansion values of the three mortars made with Type 30-1, Type 30-2 or Type 10-3 cements all exceeded the 0.04%-limit at 42 days.

§. 7.3.2. Effect of Curing Temperature

The effect of curing temperature on expansion of Type 30-1 cement mortars is shown in Fig. 7-3. The expansion developed gradually from 1 to 28 days and accelerated after 28 days for all specimens cured at 80 or 90 °C. The increase of curing temperature resulted in a significantly increased expansion of the mortars after 42 days. The expansion rate of the mortar cured at 80 °C started to decrease at about 42 days , while that cured at 90 °C was continuously high until about 70 days. The expansion values at

90 days were 0.78% and 1.38% for the mortars initially cured at 80 and 90 °C respectively.

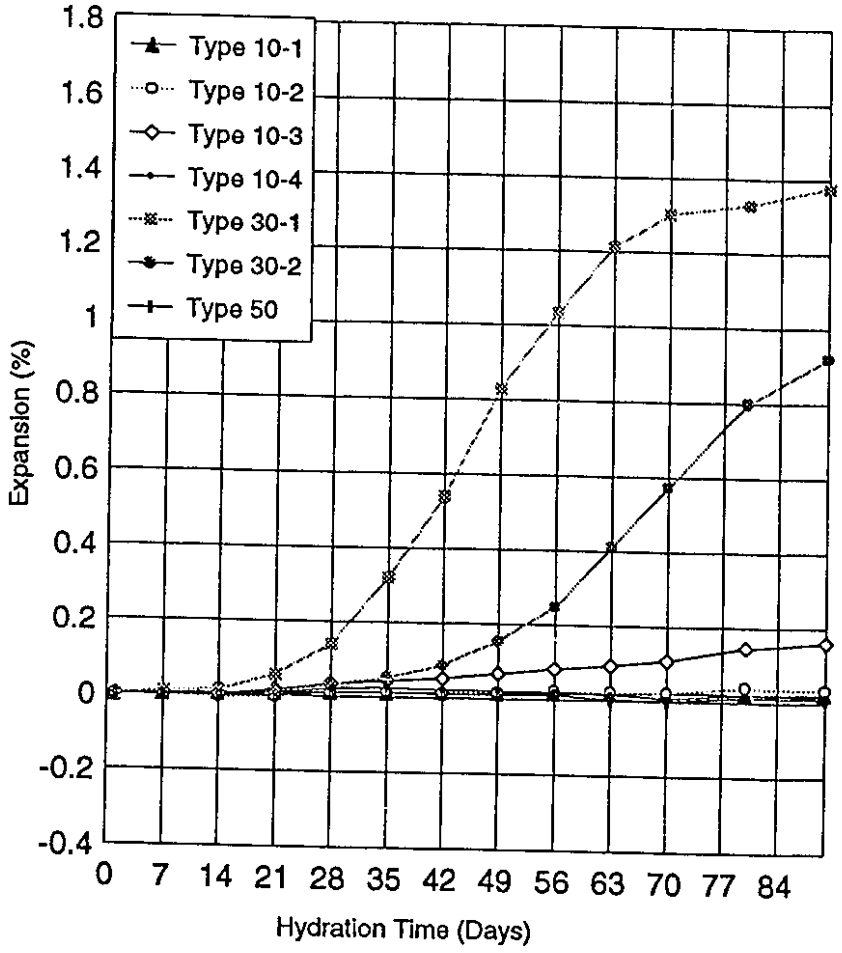


Fig. 7-1. Effect of Portland cement types on expansion of mortar cured at 90 °C.

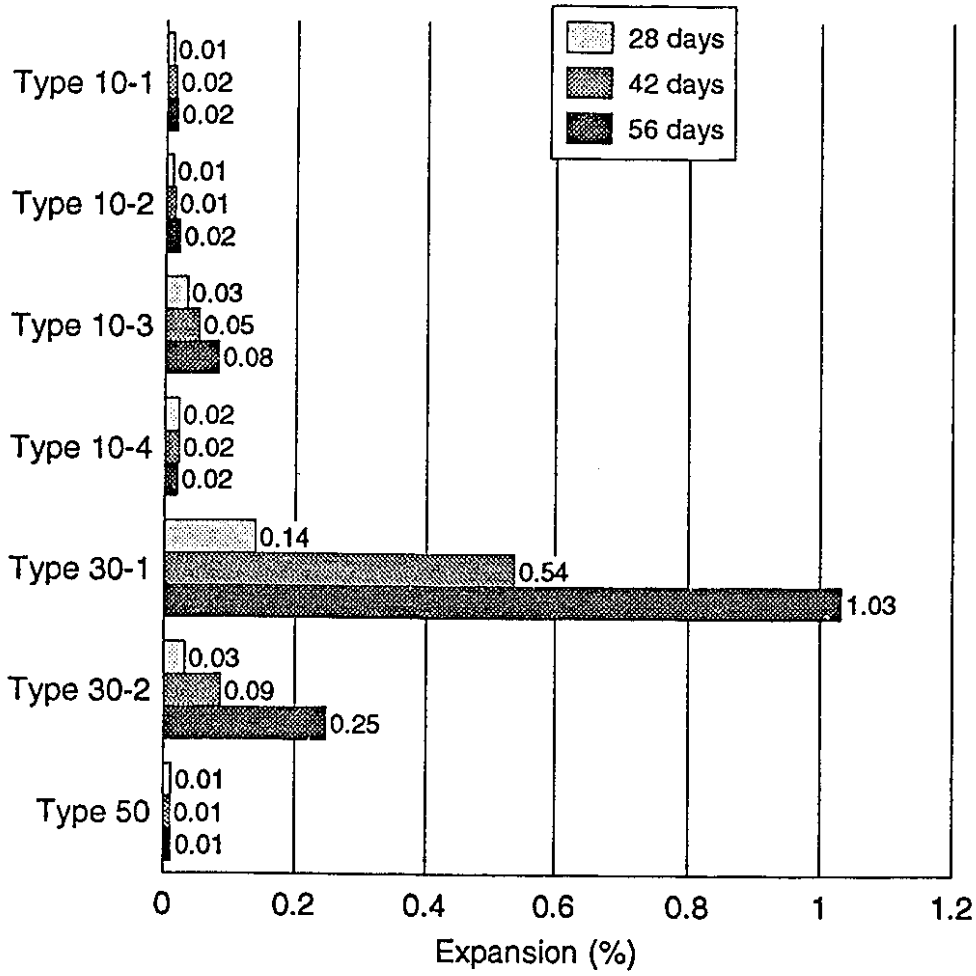


Fig. 7-2. Effect of Portland cement types on expansion at 28, 42 and 56 days.

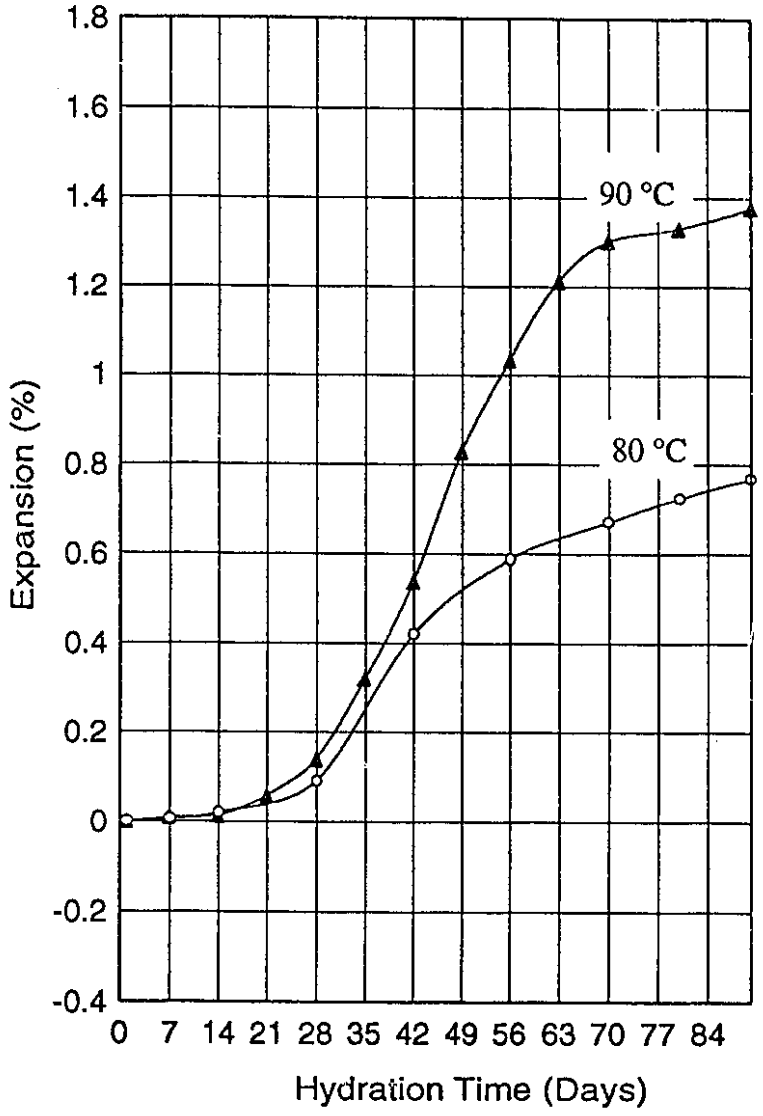


Fig. 7-3. Effect of curing temperature on expansion of Type 30-1 Portland cement mortars.

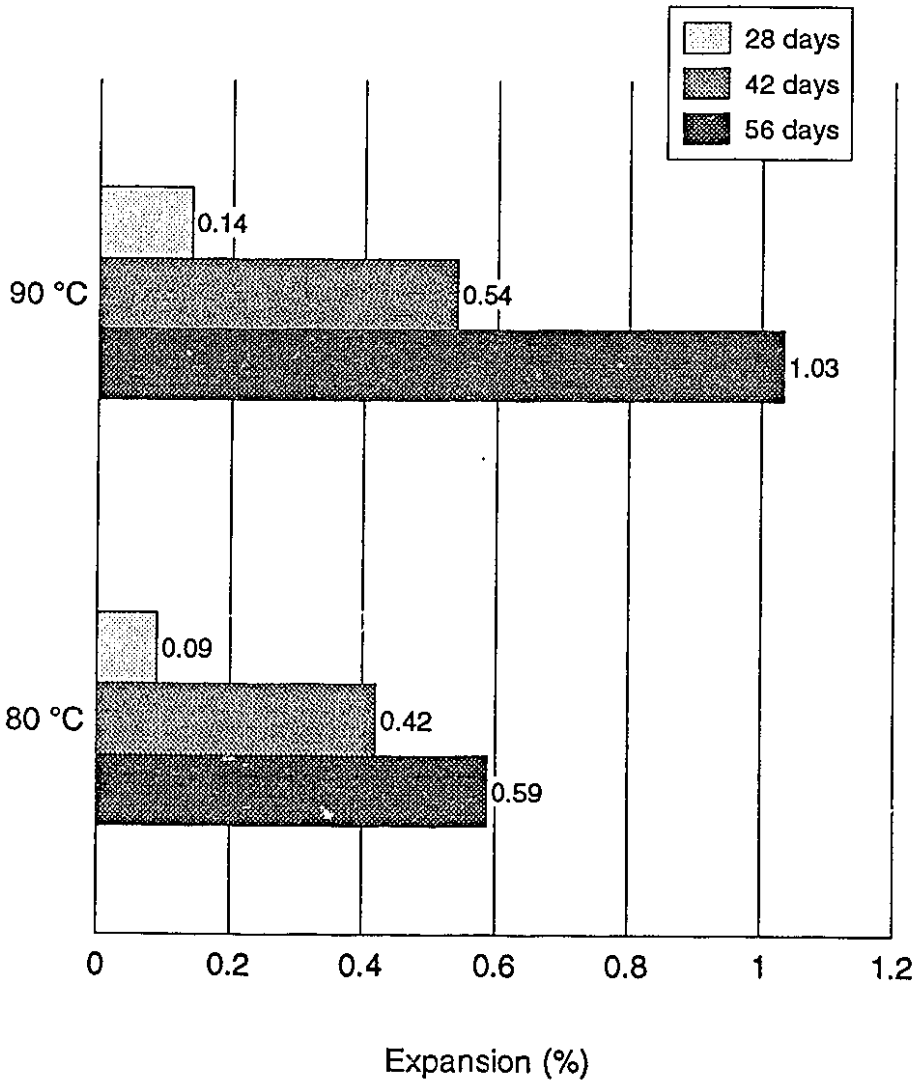


Fig. 7-4. Effect of curing temperature on expansion of Type 30-1 Portland cement mortars at 28, 42 and 56 days.

The expansion values of cement mortars at 28, 42 and 56 days are shown in Fig. 7-4. The specimens initially cured at 80 or 90 °C both exceeded the 0.04%-limit at 28 days.

§. 7.3.3. Effect of Sand Type

The effect of different types of sand on the expansion of Type 30-1 cement mortars initially cured at 90 °C is shown in Fig. 7-5. Mortars containing coarse river sand or natural river sand had higher expansion values before 42 days than those containing other sands. The expansion of the mortar containing fine river sand started to accelerate after about 35 days and reached the highest expansion value of 1.65% at 90 days. The expansion of the mortar made with 20-30 standard sand developed slowly compared to those made with river sand. It reached a value of about 1.2% at 90 days. Expansion of the mortar made with graded standard sand was much smaller than the others. It increased mainly after 42 days and reached about 0.20% at 90 days.

The expansion values of cement mortars made with different types of sand at 28, 42 and 56 days are shown in Fig. 7-6. The mortars, except those made with graded standard sand, all had expansions over the 0.04%-limit at 28days. The expansion of the mortar made with graded standard sand was less than the 0.04%-limit at 56 days.

§. 7.3.4. Effect of the Sand/Cement Ratio

The effect of the sand/cement (s/c) ratio of the Type 30-1 cement mortars initially cured at 90 °C is shown in Fig. 7-7. Similar expansion was obtained in the mortars with s/c ratio of 2.00 and 2.75. An increase or decrease of s/c ratio to 3.00 or 1.00 would reduce the expansion of the cement mortars. The effect of s/c ratio on the expansion was relatively less significant than the effect of other parameters.

The expansion values of cement mortars having different s/c ratios at 28, 42 and 56 days are shown in Fig. 7-8. The expansions of all the mortars were larger than the 0.04%-limit at 28 days.

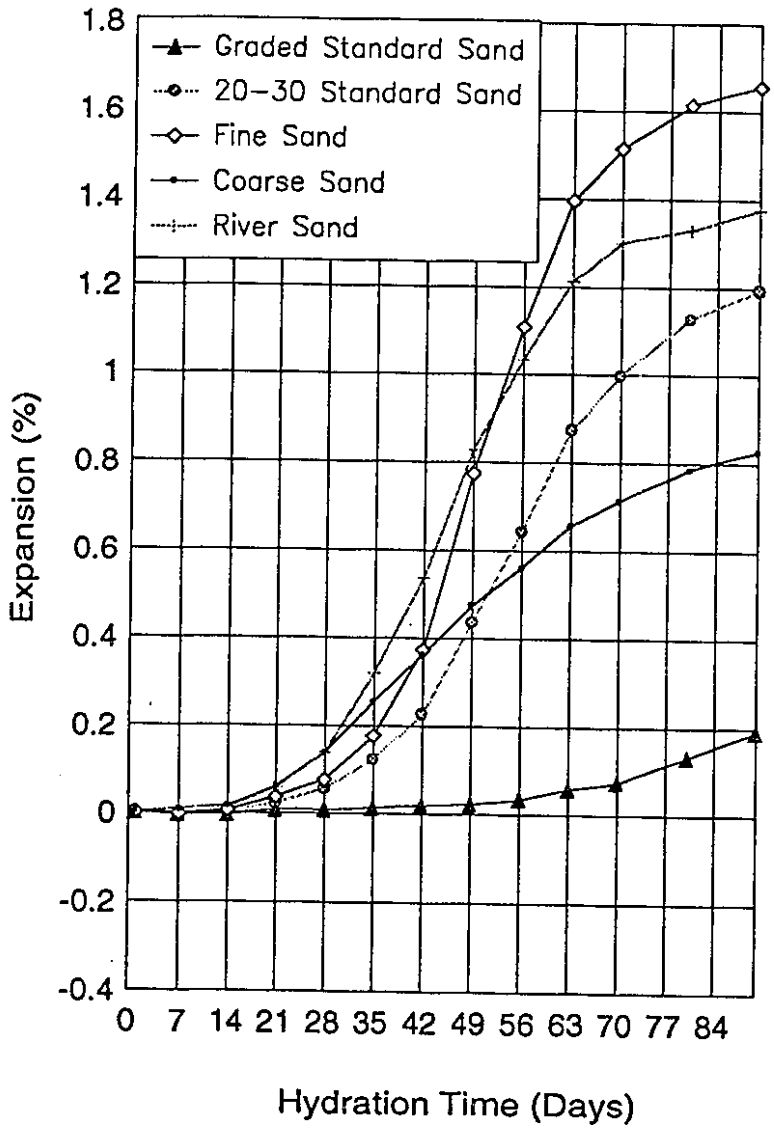


Fig. 7-5. Effect of sand types on expansion of Type 30-1 Portland cement mortars initially cured at 90 °C.

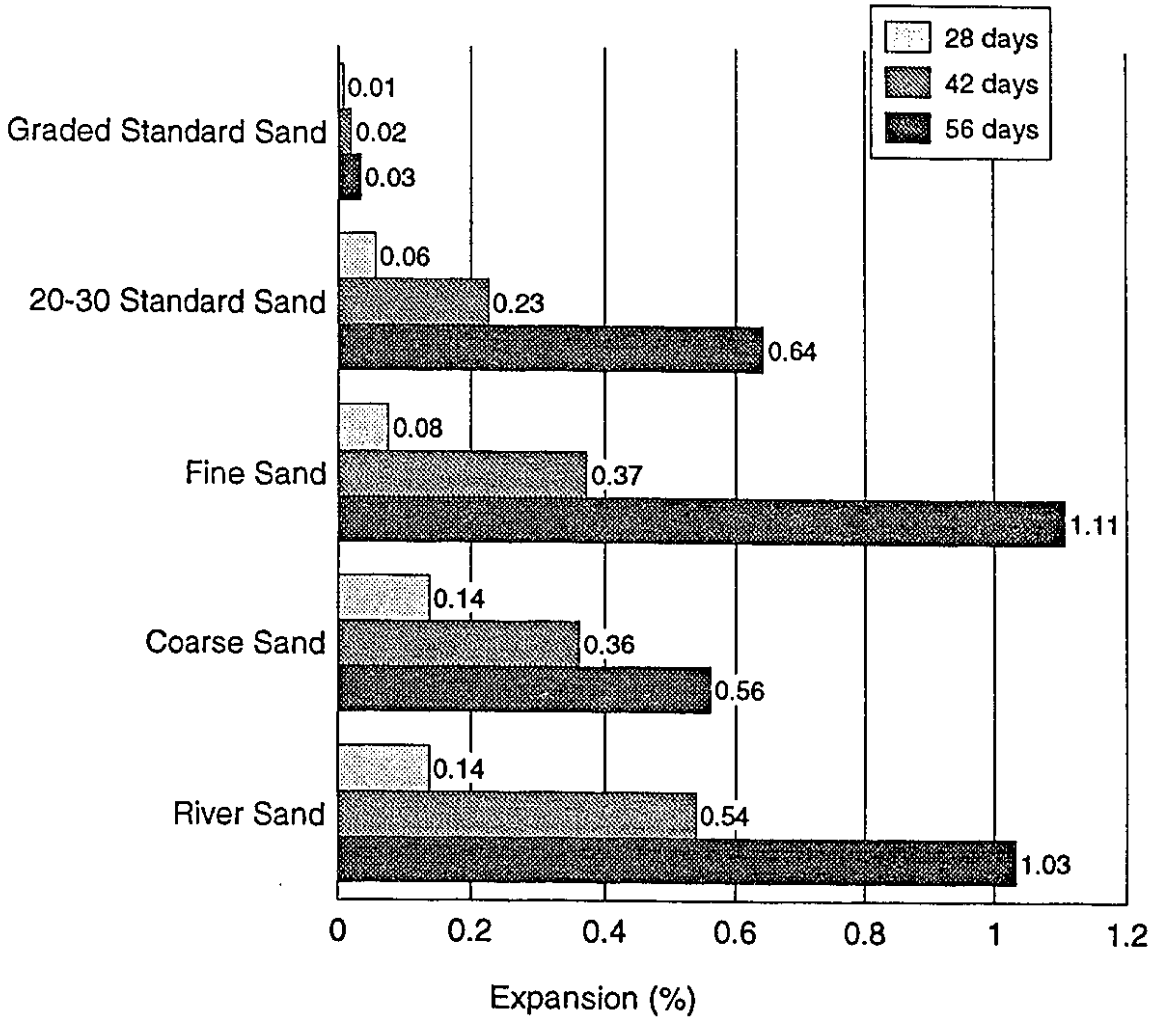


Fig. 7-6. Effect of sand types on expansion of Type 30-1 Portland cement mortars (initially cured at 90 °C) at 28, 42 and 56 days.

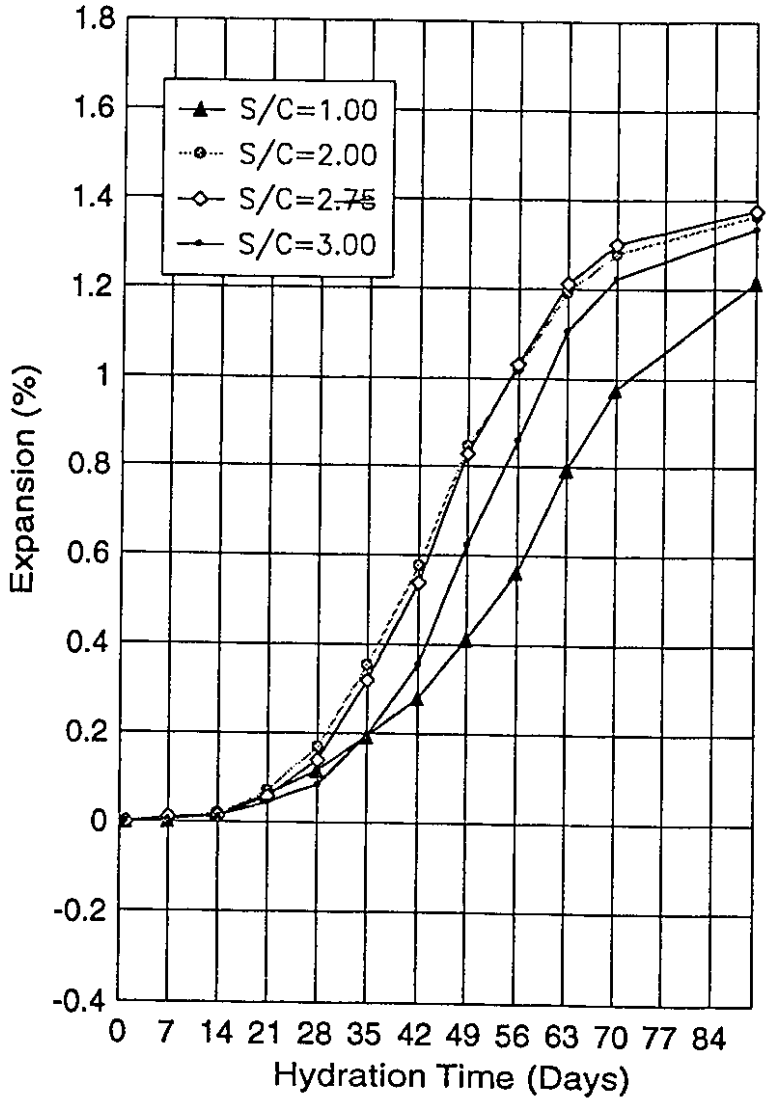


Fig. 7-7. Effect of sand/cement ratio on expansion of Type 30-1 Portland cement mortars initially cured at 90 °C.

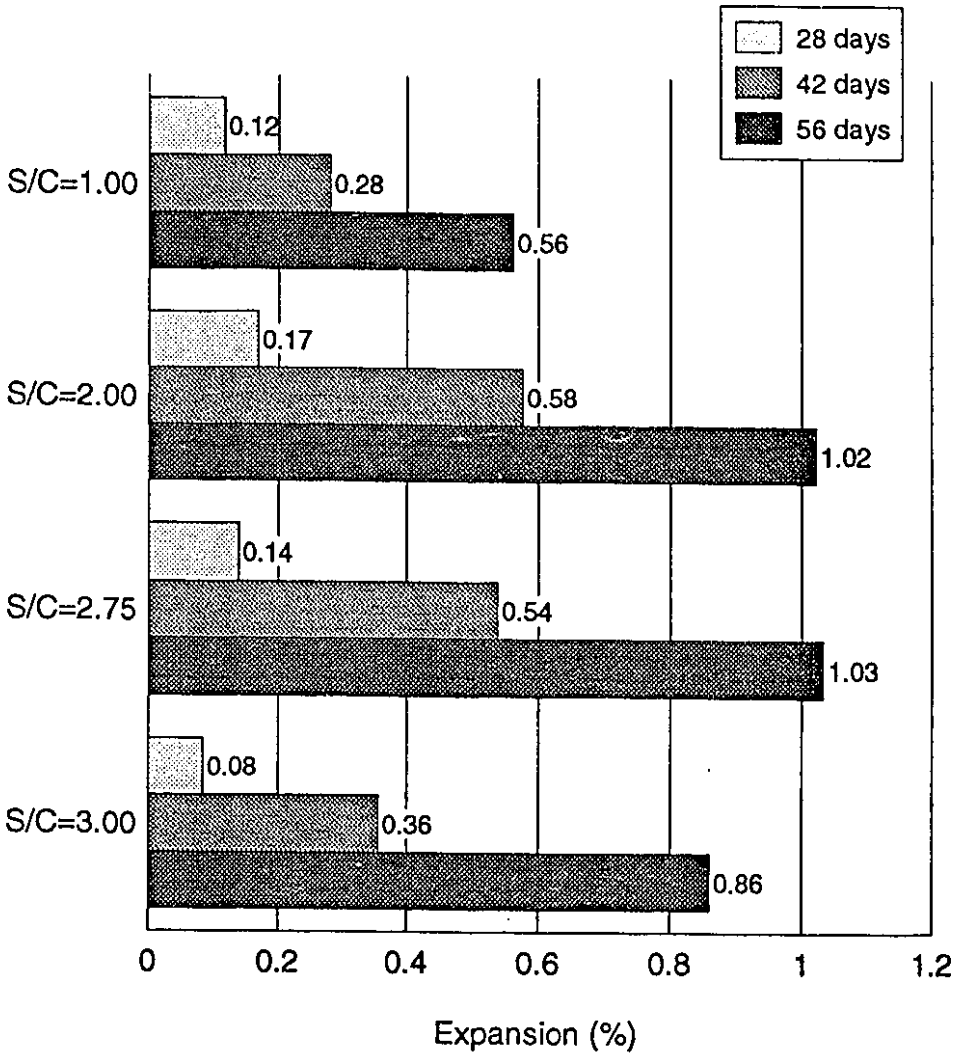


Fig. 7-8. Effect of sand/cement ration on expansion of Type 30-1 Portland cement mortars (initially cured at 90 °C) at 28, 42 and 56 days.

§. 7.3.5. Effect of Specimen Size

The effect of specimen size on expansion of Type 30-1 Portland cement mortar initially cured at 80 °C is shown in Fig. 7-9. The expansion of the large size (3x3x11-in.) specimen was less than that of the small size (1x1x6-in) specimen during the ages from 14 to 80 days. The expansion of the large size specimen exceeded that of the small size specimen after about 80 days.

The expansion values of portland cement mortar specimens with different sizes at 28, 42 and 56 days are shown in Fig. 7-10. The expansion values of the small size mortar specimen exceeded the 0.04%-limit at 28 days. Those of the large size mortar specimens were less than the 0.04%-limit at 28 days and larger than the 0.04%-limit at 42 days.

§. 7.3.6. Effect of Thermal-Drying

The effect of thermal drying on expansion of Type 30-1 and Type 10-1 Portland cement mortars initially cured at 80 °C is shown in Figs. 11 and 12. A significant increase of expansion after 28 days was found for the Type 30-1 specimens subjected to 3 or 5 drying/re-wetting cycles. An increase of the drying/re-wetting cycles resulted in a increase in the expansion of the mortars. Little or no expansion was found in any specimens made with Type 10-1 Portland cement.

The expansion values of the cement mortar specimens made with Type 30-1 or Type 10-1 Portland cement subjected to different cycles of drying/re-wetting at 28, 42 and 56 days are shown in Figs. 13 and 14. The expansions of all the mortar specimens made with the Type 30-1 cement exceeded the 0.04%-limit at 28 days. None of the mortar specimens made with Type 10-1 cement had an expansion exceeding the 0.04%-limit.

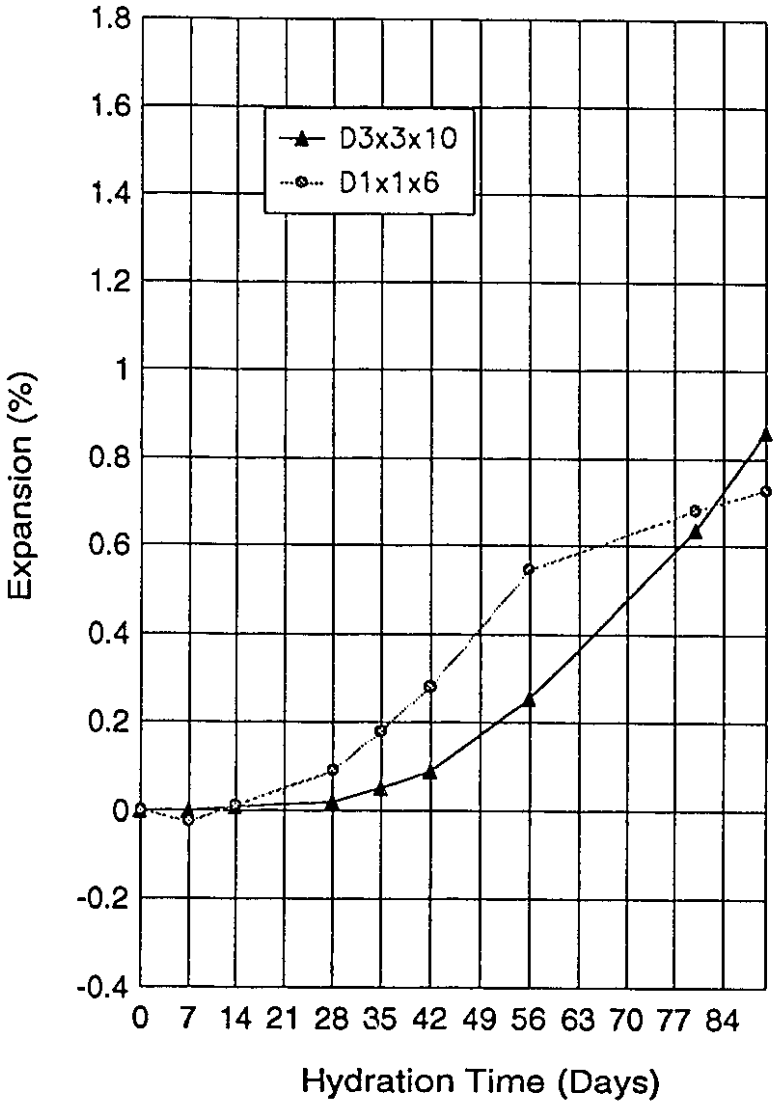


Fig. 7-9. Effect of specimen size on expansion of Type 30-1 portland cement mortars initially cured at 80 °C.

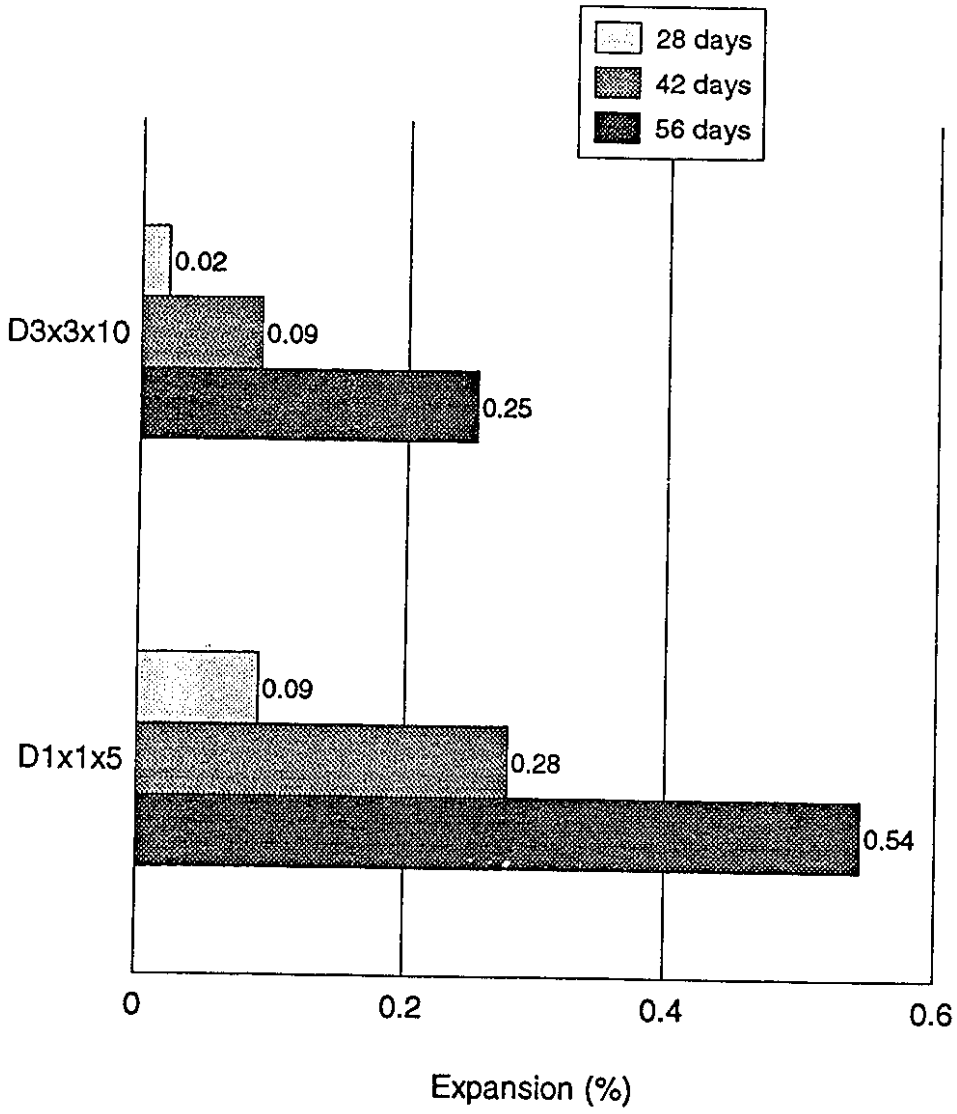


Fig. 7-10.Effect of specimen size on expansion of Type 30-1 Portland cement mortars (initially cured at 80 °C) at 28, 42 and 56 days.

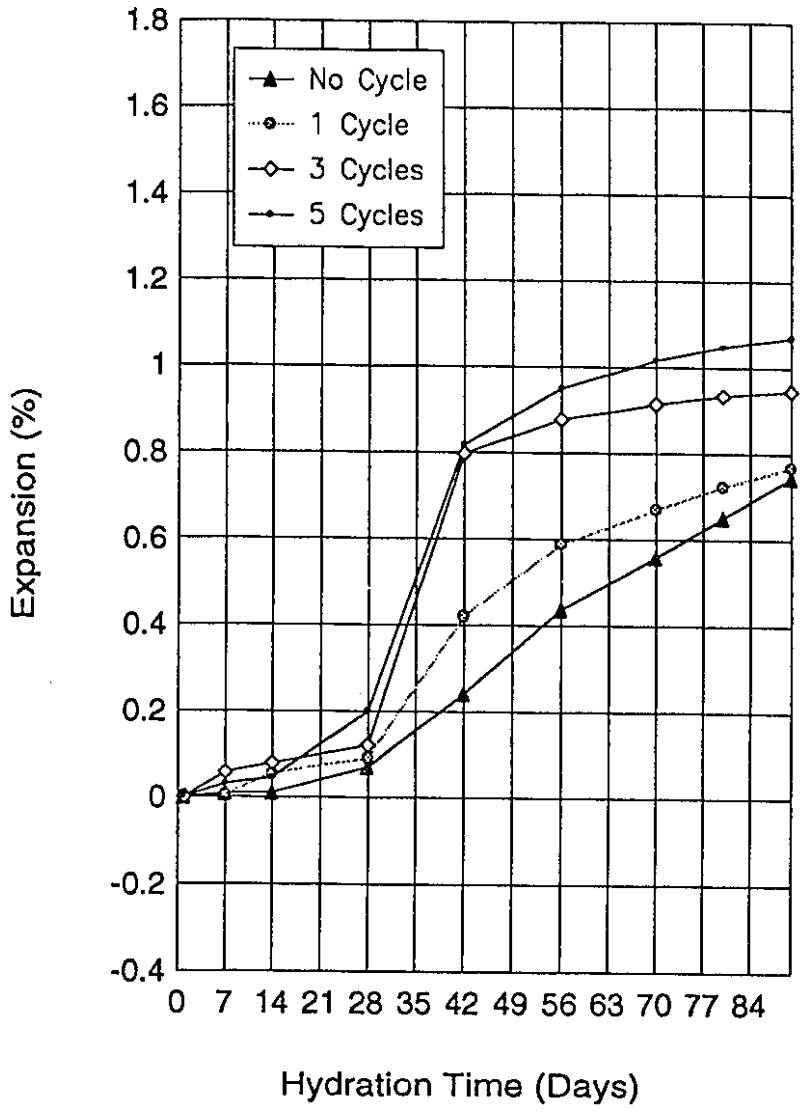


Fig. 7-11. Effect of thermal-drying on expansion of mortars made with Type 30-1 Portland cement initially cured at 80 °C.

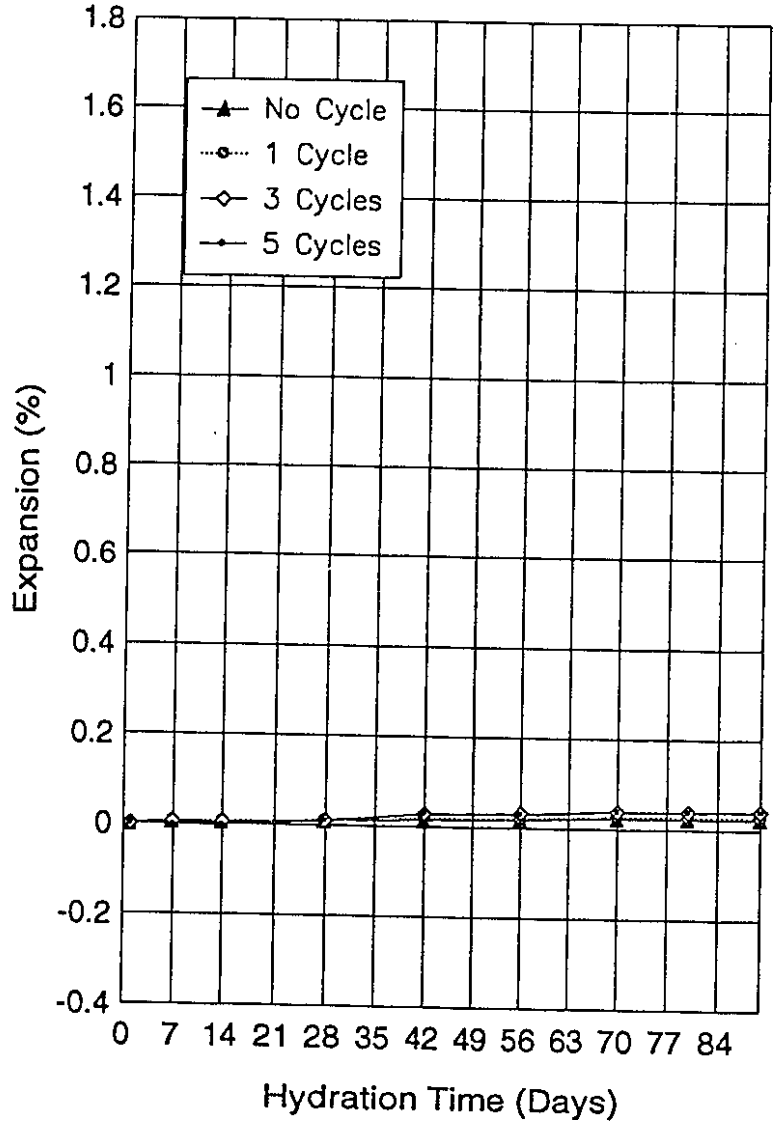


Fig. 7-12. Effect of thermal-drying on expansion of mortars made with Type 10-1 Portland cement initially cured at 80 °C.

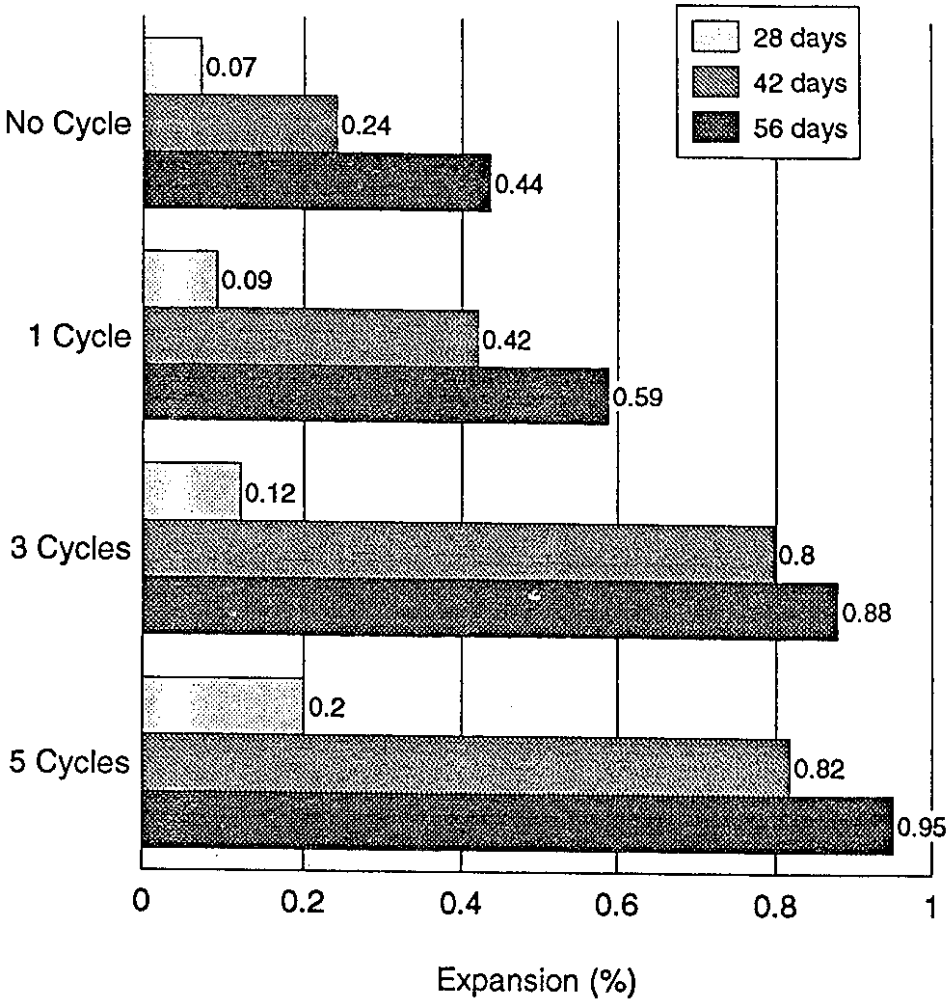


Fig. 7-13. Effect of thermal-drying on expansion of mortars made with Type 30-1 Portland cement (initially cured at 80 °C) at 28, 42 and 56 days.

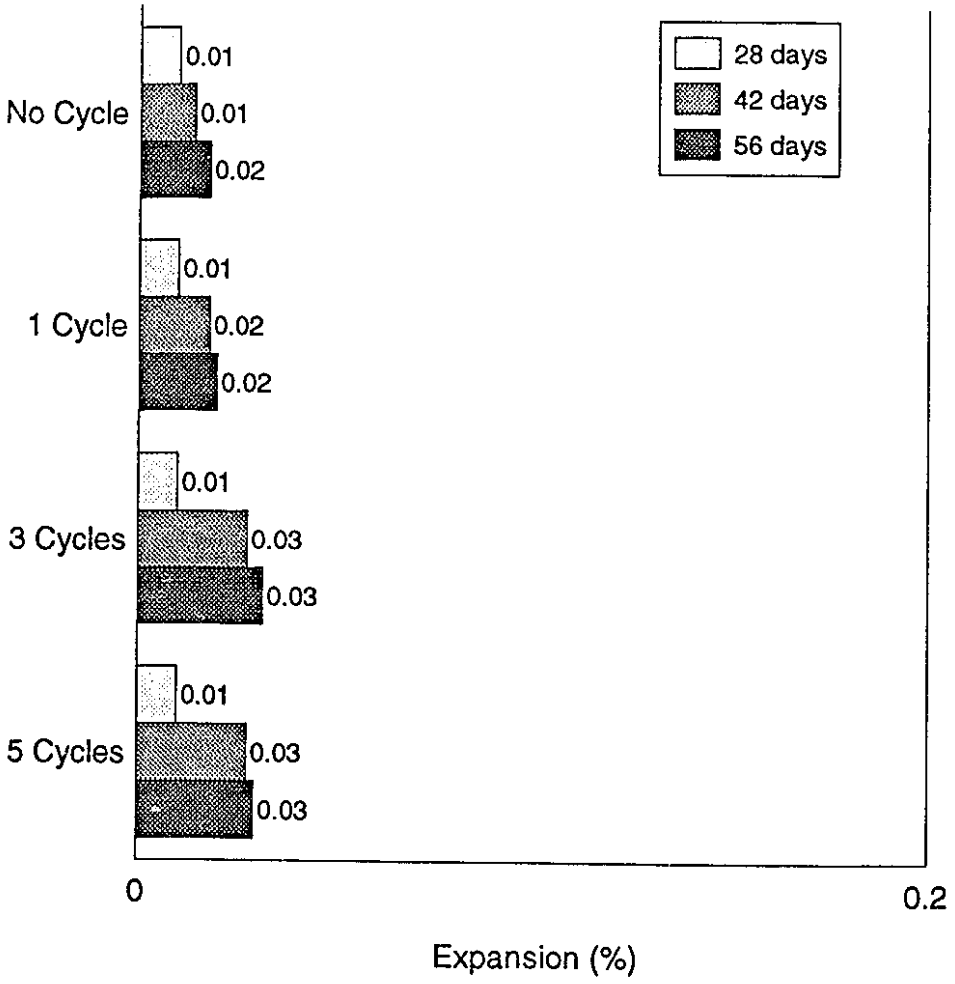


Fig. 7-14. Effect of thermal-drying on expansion of mortars made with Type 10-1 Portland cement (initially cured at 80 °C) at 28, 42 and 56 days.

§ 7.4. Discussion

§ 7.4.1. Test for Delayed Ettringite Formation Potential

The objective of the test method is to demonstrate the potential for delayed ettringite formation (DEF) of a given portland cement. This test method activates the mechanisms responsible for DEF in portland cement products which are initially moist-cured at high temperature. The conditions required for DEF can be summarized as follows:

(1) an optimum oxide and mineral composition, e.g. high content of SO_3, Al_2O_3, and C_3A.

(2) a high value of fineness, e.g. higher than 5000 cm^2/g.

(3) short pre-storage periods, e.g. less than 2 hours.

(4) high temperature moist-curing, e.g. higher than 75 °C.

(5) pre-existing cracks so that ettringite can preferentially form in the cracks. This requires less surface energy than for ettringite formation in the bulk cement paste matrix.

(6) a moist service environment.

Conditions 1 and 2 are characteristics of the test cement. Conditions 3 to 6 are provided by the test method.

Reaction between sulphate and C_3A to form AFt in a hydrated portland cement occurs at very early ages. A short pre-storage period prevents complete consumption of the sulphate. The remaining sulphate, or sulphate from decomposition of the calcium sulphoaluminate hydrates (e.g. AFt), will be rapidly adsorbed by C-S-H gel forming "phase X" in the cement product when high temperature moist-curing follows. Therefore, an internal sulphate source for DEF is formed in the cement products. Sulphate adsorbed by C-S-H gel at high temperature will be released slowly at later ages when the cement

products are placed in a moist environment (e.g. out-door panels and rail-way sleepers). Pre-existing cracks can accelerate the nucleation of ettringite crystals. Nucleation of a crystal requires less surface energy in a crack than in the cement paste matrix. Pre-existing cracks can be induced by a weathering process. Out-door structures may experience thermal drying. The surface temperature of a concrete product under solar radiation can be higher than 80 °C in the summer. Sulphate ions, after release from the C-S-H gel, will diffuse into the nearest microcrack and react with the Al-bearing materials in the crack to nucleate and crystallize ettringite. Growth of ettringite crystals opens the crack and damages the cement products. A cement product having no pre-existing crack may also suffer deterioration due to DEF, but it requires more energy and thus longer time.

§ 7.4.2. Critical Conditions and Procedures in the Test Method

Some test conditions and procedures are critical for DEF in portland cement products. These are discussed as follows:

(1) Pre-storage time

The pre-storage time is a critical parameter determining the severity of the test method. It has been reported that a prolonged pre-storage time (e.g. longer than 2 hours), before the high temperature curing, would minimize the DEF-induced expansion in a pre-cast concrete product. Long pre-storage time allows sulphate to completely react with C_3A forming ettringite. This reduces the amount of sulphate available for adsorption by C-S-H gel during the high temperature curing. One hour pre-storage was used in this study.

(2) Curing Temperature

The curing temperature determines the expansion rate and amount of expansion of a portland cement product due to DEF. Increase of curing temperature (e.g. from 65 to 95 °C) would significantly accelerate the expansion rate and enhance the final expansion

value. A curing temperature as high as reasonably possible (e.g. 95 °C) is suggested for a rapid test method.

(3) High Temperature Curing Period

Prolonging the high temperature curing period would increase the ultimate expansion of a portland cement product. A long period of high temperature curing enhances the decomposition of AFt or AFm phases and the degree of sulphate adsorption by C-S-H gel. The potential of this internal sulphate source for DEF is determined by the amount of sulphate adsorbed by the C-S-H gel. Twelve hours of high temperature curing may be selected for a rapid test method.

(4) Thermal Drying Pre-treatment

The thermal drying pre-treatment simulates the weathering process that creates microcracks in the portland cement products after high temperature curing. This treatment is mainly a crack-making process rather than a phase-changing process. The dissolved sulphate has been adsorbed by the C-S-H gel after the high temperature curing. Further decomposition of calcium sulphoaluminate hydrates (e.g. AFm phase) may still occur, but the amount of released sulphate will be very small. Sulphate is difficult to release from the C-S-H gel during drying. One thermal drying/re-wetting cycle may be used in a rapid test method.

(5) Sand Types

Different sand types will give different expansion characteristics of a portland cement mortar due to DEF. Expansion develops more rapidly in the mortar made with coarse sand than with fine sand. Mortar made with natural river sand has a higher expansion value than that made with the standard sand. River sand is not suitable for a standard test method since its characteristics are altered with different batches. A 20-30 standard (silica) sand (conforming to ASTM C 778) can be selected for a standard test providing a high enough expansion occurs in a reasonably short period.

This test method may be useful in evaluating a cement for use in the precast concrete structures which will experience out-door weathering, even though the test parameters (related to the above critical conditions and procedures) used in this proposed test method (e.g. one hour pre-storage, 14 hours moist-curing at 95°C and 24 hours drying at 85 °C) are more severe than those that occur in some precast concrete production. It appears that only some of the cements (e.g. Type 30 cements in this study) have the potential for DEF expansion. Selection of a durable cement will benefit both the cement producer and the cement user.

§ 7.4.3. Expansion/Time Criteria

The expansion/time criteria are, based on the data provided in this study, difficult to determine. These data may however be useful in developing the framework for a method based on more test data. The 90-day expansion was plotted vs 28-, 42- and 56-day expansion in Fig. 7-15. The diagram can be divided into four regions:

(i) Region A; both the 90-day expansion and the 28-, 42- or 56-day expansion do not exceed 0.04%. Therefore, a cement in this region is free of DEF expansion.

(ii) Region F; both the 90-day expansion and the 28-, 42- or 56-day expansion exceed 0.04%. Therefore, a cement in this region is susceptible to causing expansion due to DEF.

(iii) Region X; the 90-day expansion exceeds 0.04%, but the 28-, 42- or 56-day expansion does not exceed 0.04%. This indicates that the expansion of this cement mortar is much delayed. Further length measurements are required for longer terms.

(iv) Region Y; the data in this region are not realistic, since the expansion at 90 days should not be smaller than those at earlier ages.

Several 28/90-day expansion points were positioned in the Region X. This indicates that a high possibility of failure at 90 days exists for the cement even though the corresponding 28-days expansion did not exceed the 0.04%-limit. The 28-day expansion

value does not appear to be suitable for determining the DEF potential of a given cement. No 42/90-day and 56/90-day data points (except one specimen made with graded standard sand) are in the Region X. The expansion at 90 days will also not exceed 0.04%, if a cement does not exceed the 0.04%-limit at 42 days. Therefore this cement can be generally considered to be free of DEF (Region A). A large expansion is expected at 90 days (Region F), if a cement exceeds the 0.04%-limit at 42 days.

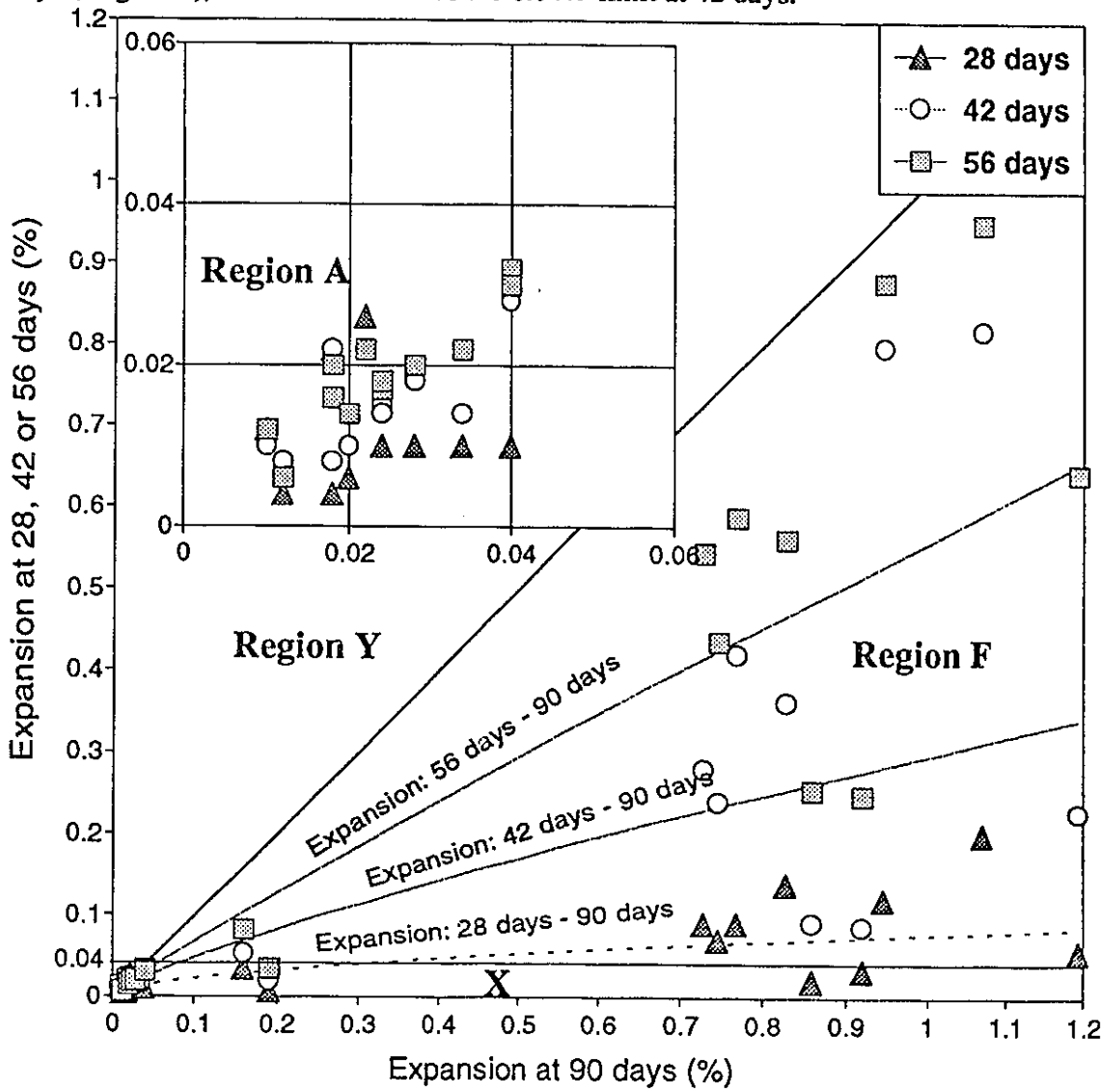


Fig. 7-15. Expansion of cement mortars: 90 days vs 28, 42 and 56 days. Data obtained using the eight cements studied.

§ 7.4.4. Differences between the Duggan Test and the Proposed Test Method

An accelerated test method, the Duggan test (Grabowski et al. 1992), was reported to examine the expansion potential of concrete cores drilled from concrete products or structures. The test involves several thermal-drying/re-wetting cycles followed by length-change measurements on concrete cores stored in water. The concretes may, or may not, be cured initially at a high temperature. Therefore, the internal source of sulphate may not be the same as that formed in high temperature moist-cured concrete. It is more likely to be in the form of calcium sulphate solid formed by decomposition of the calcium sulphoaluminate-sulphate phase, e.g. AFt or AFm. The C-S-H gel may not be able to adsorb sulphate since phase X is difficult to form in a relatively dry condition typical of that resulting from the drying process of the Duggan test. Sulphate ions from calcium sulphate upon re-wetting can readily migrate into the nearest cracks, react with the aluminate phase and re-crystallize in the form of ettringite.

The two terms "secondary ettringite formation (SEF)" and "delayed ettringite formation (DEF)" are often used and confused. They both occur in actual concretes under different conditions. A comparison of the SEF and DEF is provided in Table 1.1. (see Chapter 1). Therefore in the Duggan test, the terminology "SEF" appears more suitable than "DEF". However, the expansion of concrete in the Duggan test could be a single result of SEF or the total result of both SEF and DEF. The Duggan test over-estimates the deterioration potential of DEF. It is therefore a very severe test method for steam-cured pre-cast concrete products. Oberholster et al. (1992) argued that on the basis of their investigation, the Duggan test showed that all tested concrete slèepers were potentially subject to deleterious expansion. However, some of the sleepers did not show any signs of cracking after more than 10 years of service. Idorn and Skalny (1993) doubted that a high expansion potential indicated by the Duggan test (even when the curing temperature of the precast concrete products did not meet the critical condition for

DEF) was realistic. The Duggan test creates microcracks simulating an accelerated weathering process. It also creates an extra internal sulphate source for "secondary" ettringite formation, which may not originally exist in the concrete. Aluminate hydrates combine with sulphates to form AFt or AFm phases in normal temperature cured concrete at early ages. They are essentially stable in the Portland cement concrete if no severe thermal treatment is applied. DEF usually does not occur in concrete cured at normal temperature. Severe thermal treatment, e.g. that characterized by the Duggan test, can decompose stable calcium sulphoaluminate-sulphate in concrete members, forming an unstable internal sulphate source. An internal sulphate source for DEF forms during the initial high temperature moist-curing period. An internal sulphate source for SEF is created during certain extra thermal treatment, e.g. in the Duggan test. Therefore, the concrete passing the Duggan test is believed to have no potential for DEF; the concrete not passing the Duggan test may or may not suffer from the DEF problem.

§ 7.5 Conclusions

1. The proposed test method can be used to determine the expansion potential, due to delayed ettringite formation (DEF), of the cement mortar (made with a Portland cement) initially moist-cured at high temperature.
2. The critical conditions in the proposed test method are a curing temperature over 90 °C, a 14-hour curing period and less than one hour pre-storage at ambient temperature..
3. A 20-30 standard sand conforming to ASTM C 778 is suggested for use in making mortar specimens for the proposed test method.
4. A thermal drying pre-treatment of mortar specimens after the high temperature curing step in the proposed test accelerates the expansion due to DEF.

5. An expansion of mortar not exceeding 0.04% at 42 days when the mortar is subjected to the proposed test method may be considered as a suitable criterion for determining the DEF potential of a given Portland cement.

Chapter 8

PREVENTIVE MEASURES TO REDUCE THE DETERIORATION OF PORTLAND CEMENT PRODUCTS DUE TO DELAYED ETTRINGITE FORMATION

- Effect of Siliceous Materials on Expansion due to DEF

- Microfibre Reinforcement Using Natural Wollastonite

§ 8.1. Introduction

Selection of a DEF-free cement by a suitable test method such as that described in Chapter 7 is of benefit to both the concrete producer and user. However in some cases an acceptable cement may be not available or there is insufficient time available for testing. Preventive measures to reduce or eliminate the deleterious expansion of a cement product due to DEF are desirable. This Chapter reports studies on the effect of some mineral additives on the expansion of mortars containing a DEF-suspect cement. The mineral additives include ground granulated blastfurnace slag (ggbs), Class F fly ash, Class C fly ash, silica fume, natural zeolite and natural wollastonite.

§ 8.2. Experimental

§ 8.2.1. Materials

The materials used in this research include:

(1) Type 30 Portland cement.

(2) Siliceous materials: Class F fly ash, Class C fly ash, ground granulated blastfurnace slag, silica fume and natural zeolite. The natural zeolite contains mainly clinoptilolite and gismondine. The oxide compositions of the Type 30 cement and siliceous materials are listed in Table 8.1.

(3) Wollastonite mineral microfibre.

(4) Natural River Sand: The grading curve of the sand is shown in Fig. 8-1.

Table 8.1. Oxide Composition of Cements and Siliceous Materials

	Oxide Compositions (mass %)						
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O+K_2O	SO_3
Type 30 PC	20.2	6.1	63.0	2.7	0.5	1.1	3.1
Class F fly ash	49.7	26.9	3.4	8.5	1.6	5.7	1.2
Class C fly ash	49.9	20.9	12.3	4.9	2.9	6.1	1.1
ggbs	35.4	10.5	36.7	1.0	13.4	-	1.5
Zeolite	65.7	12.5	2.0	1.7	0.9	3.2	-
Silica Fume	95.2	0.2	0.2	0.1	0.2	0.4	0.1

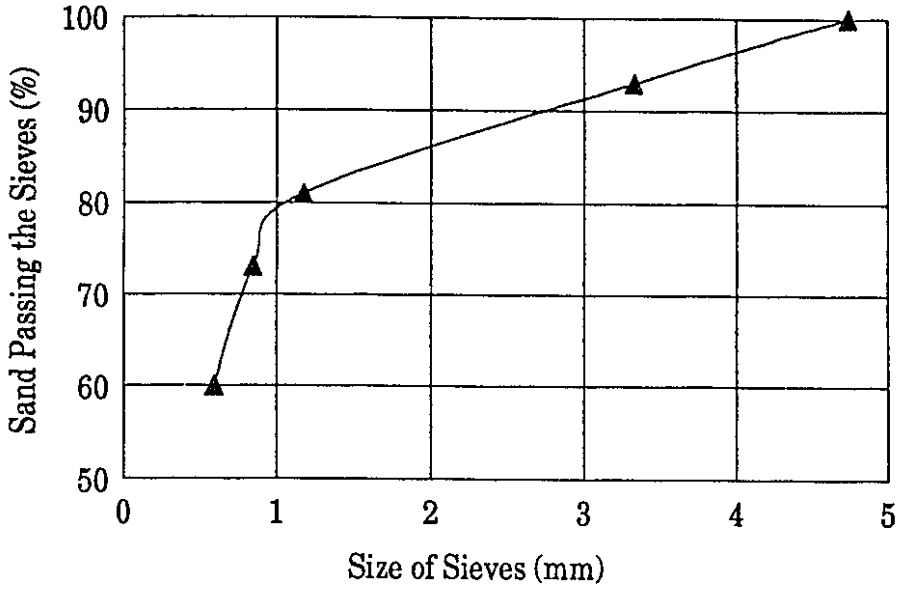


Fig. 8-1. Grading curve of river sand.

§ 8.2.2. Mix Design

Cement mortars were used in this research. The water/solid (cement+siliceous material) was 0.48. The sand/cement ratio was 2.75. Natural river sand was used. Specimens containing 30% ggbs, Class F fly ash, Class C fly ash or natural zeolite and 70% Type 30 portland cement by mass were prepared. Specimens containing 15% silica fume and 85% Type 30 portland cement by mass, and control specimens with plain Type 30 portland cement were also prepared. Addition of wollastonite microfibre was 0, 10, 20 and 30% by mass of cement. The sand was replaced by the addition of the same volume of wollastonite microfibre. The densities of the river sand and wollastonite are 2.56 and 2.90 respectively.

§ 8.2.3. Specimen Preparation

The mortars were mixed using the procedure described in Method C 305. Two 1x1x6-in. or 3x3x11-in test specimens for each cement were prepared. The temperature of the molding room, dry materials, and mixing water was maintained at 74.4°F (23 °C) and the relative humidity of the molding room was about 50%.

The specimens were placed in the moist room after casting. All test specimens in the molds were kept in the moist room for 1 hour with upper surfaces exposed to the moist air but protected from dripping water. The specimens were put in a plastic container after pre-storage. The container with test specimens was tightly covered and sealed. The container was placed in an oven. Temperature in the container was raised to 90°C in 60 min and maintained for 12 hours. The heating unit was turned off at 12 hours and the test specimens were cooled for 4 hours by opening the oven door. The specimens were removed from the molds, properly identified, and placed in water maintained at 73.4°F (23°C) for 6 hours prior to making the initial length measurement. The relative humidity in the container was maintained at 100%. The specimens were dried in an oven maintained at 85°C for 24 hours, and then cooled to room temperature after the initial

length measurement. The specimens were then stored in saturated lime water in a tank in the moist room at 23°C.

The specimens were removed from water storage, and wiped with a damp cloth before measuring. Length was measured with an electronic length comparator. The first reading on the test specimens was made at the age of 24h from the time the cement and water were mixed together. Subsequent measurements were made every 7 days. The average expansion of two specimens was reported.

§ 8.3. Test Results

The effect of addition of siliceous materials on the expansion of Type 30 cement mortars initially cured at 90 °C is shown in Fig. 8-2. Addition of any siliceous materials could significantly reduce the expansion of the mortar made with a DEF-suspect cement. Class F fly ash and ggbs were the most effective mineral additive for eliminating expansion in portland cement mortars due to DEF. Silica fume was also good for this purpose. However, the addition of silica fume was limited to 15% by mass of cement in this test because of its adverse effect on the workability (the addition of other siliceous materials was 30% by mass of the cement). Natural zeolite and Class C fly ash were relatively less effective in reducing the expansion than ggbs, Class F fly ash and silica fume.

The expansion values of cement mortar specimens containing different siliceous materials at 28, 42 and 56 days are shown in Fig. 8-3. The expansion values of the mortar specimen containing Class F fly ash and ggbs did not exceed 0.04% at ages of 28, 42 and 126 days. The expansion of Class C fly ash mortar exceeded 0.04% at 42 days. The mortar containing silica fume had an expansion larger than 0.04 at 28 days. The mortar containing a zeolite additive had expansions larger than the mortars containing any other siliceous materials.

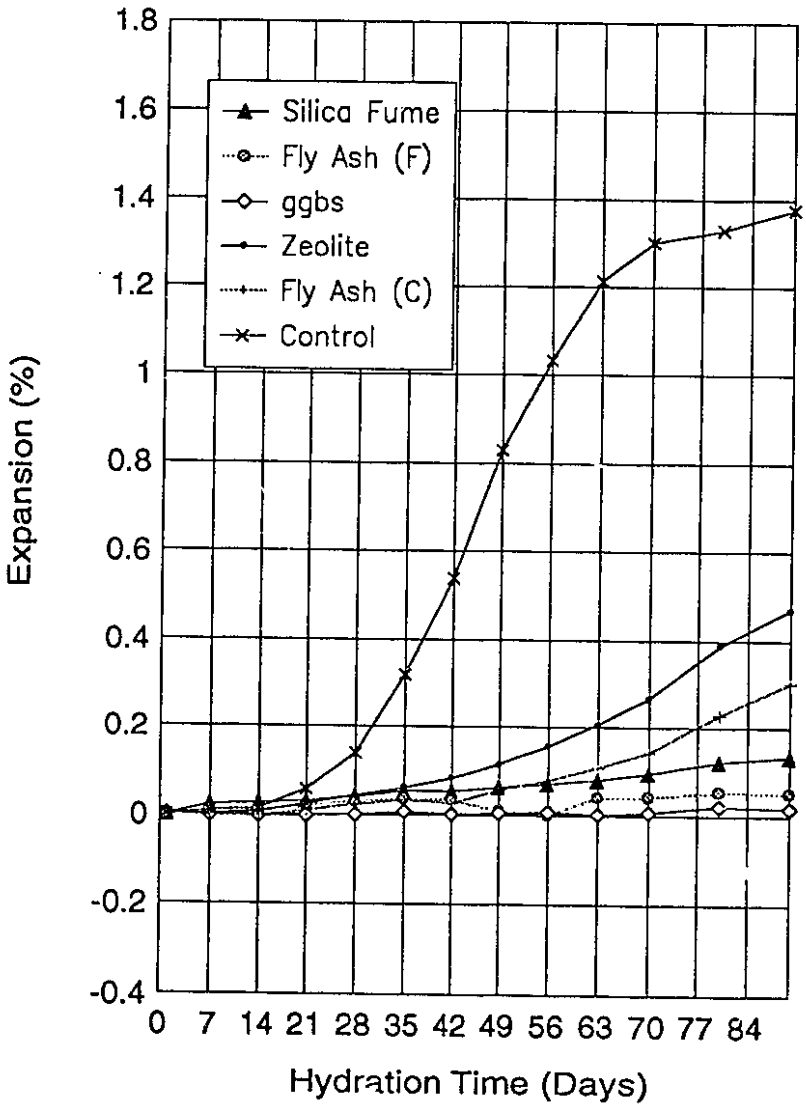


Fig. 8-2. The effect of addition of siliceous materials on the expansion of Type 30 cement mortars initially cured at 90 °C.

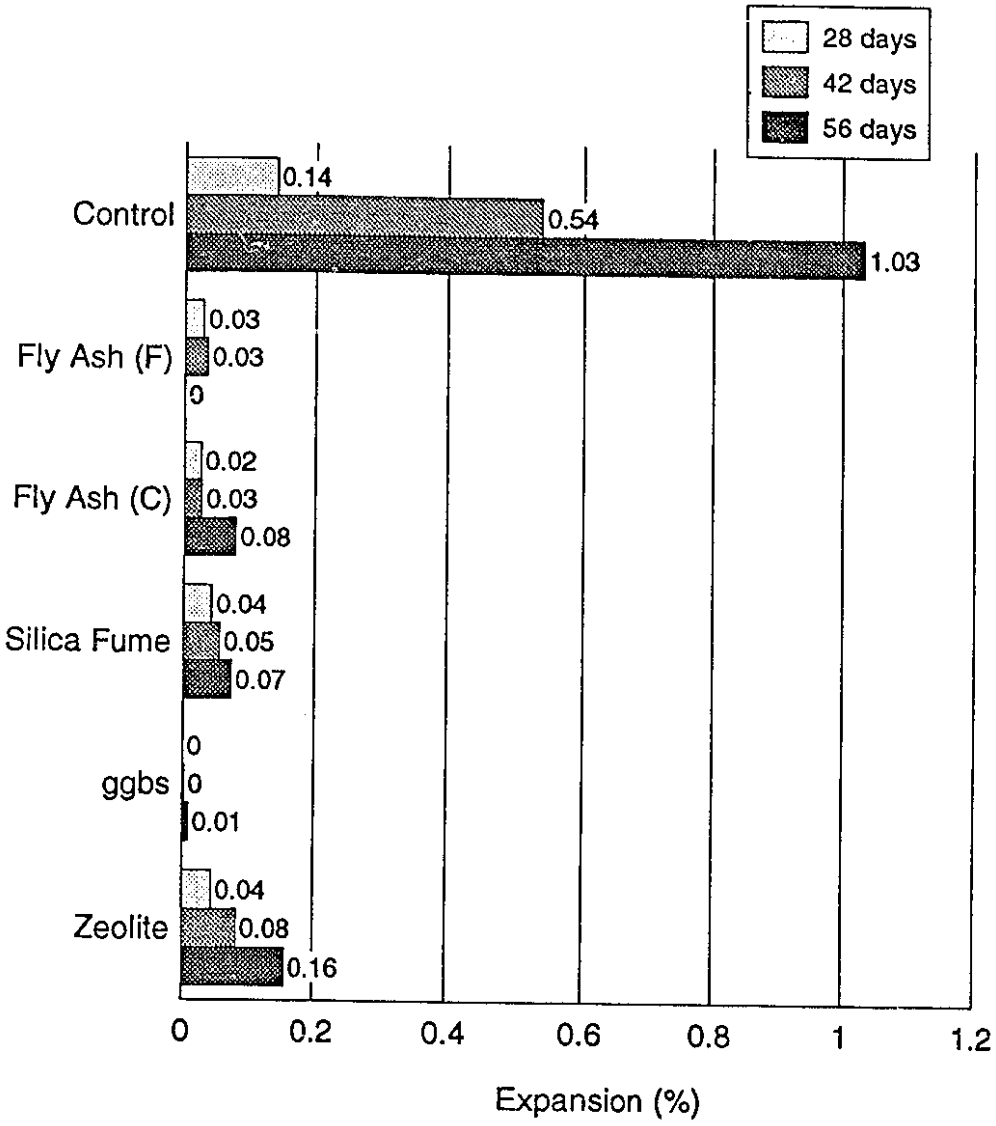


Fig. 8-3. The expansion of cement mortar specimens containing different siliceous materials at 28, 42 and 56 days.

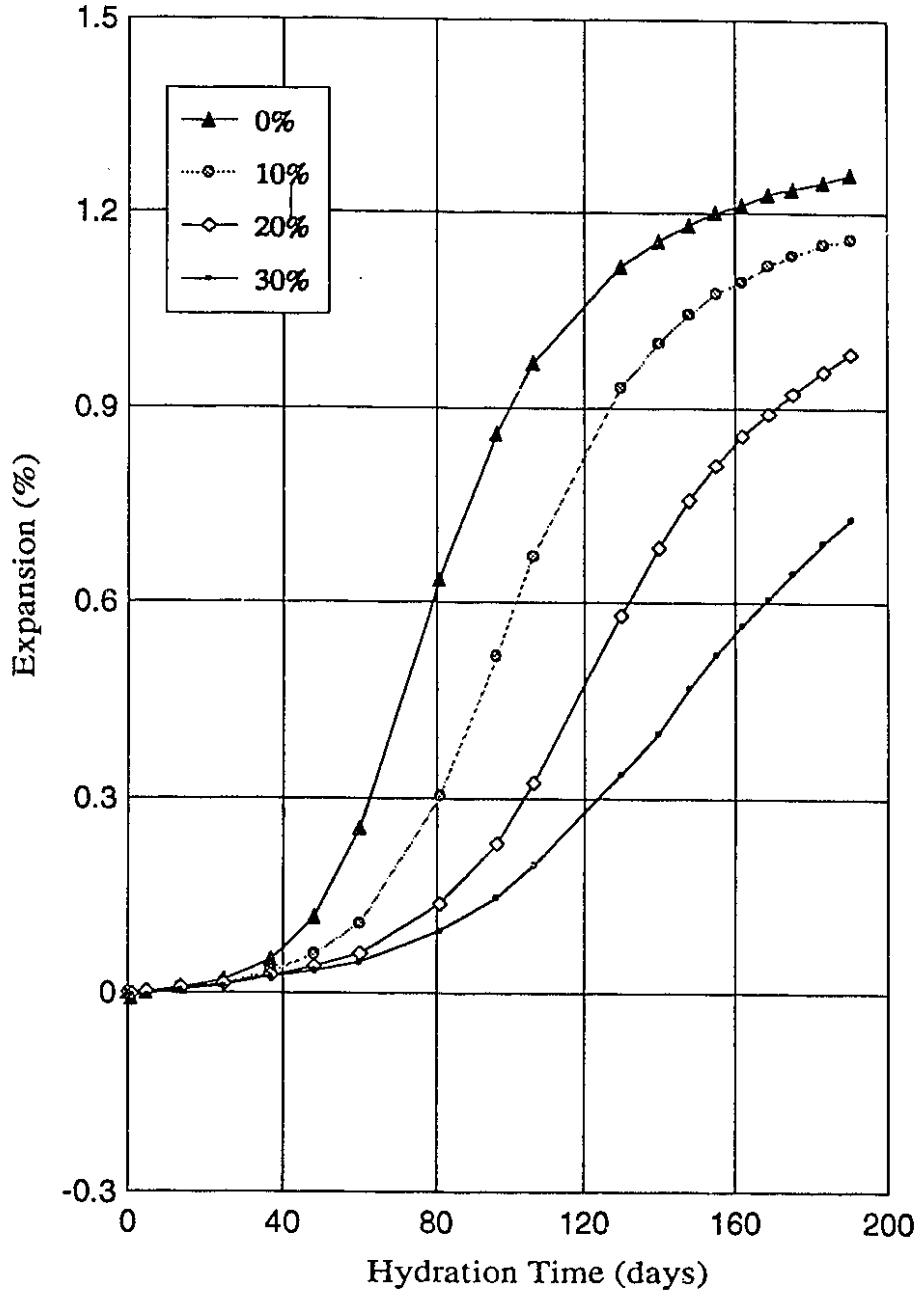


Fig. 8-4. The effect of wollastonite addition on expansion of a Type 30 cement mortar (specimen size 1x1x6 in.) moist-cured at 80 °C.

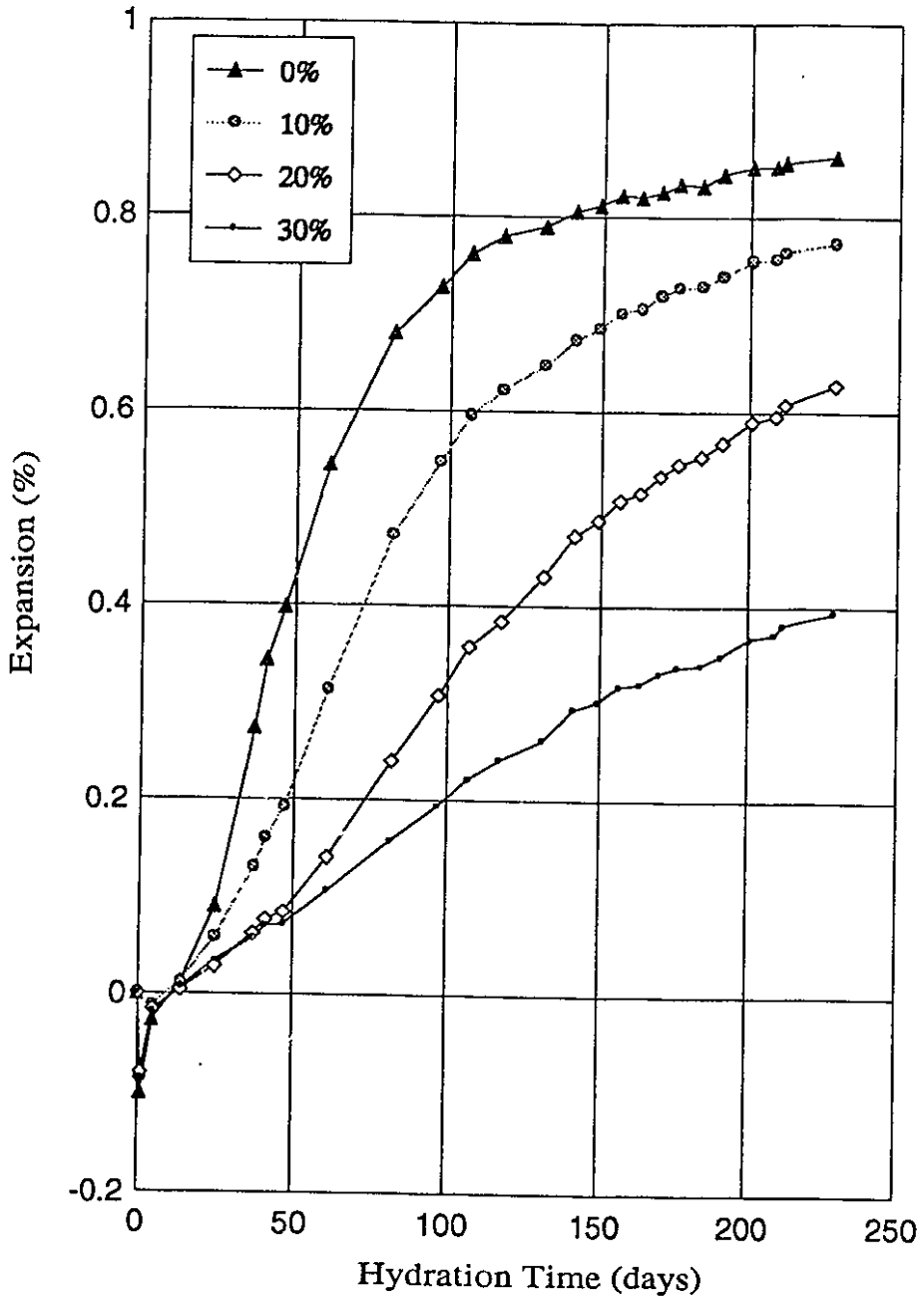


Fig. 8-5. The expansion of mortars containing wollastonite microfibre (specimen size 3x3x11 in).

The effect of wollastonite addition on the expansion of a Type 30 cement mortar moist-cured at 80 °C is shown in Fig. 8-4. The specimen size of the mortars was 25x25x125 mm. The expansion value of the cement mortar due to DEF was greatly decreased by using wollastonite microfibre. The wollastonite significantly suppressed the expansion of the cement mortar especially before 84 days. The expansion rate of the plain Type 30 cement mortar was high before 84 days and then started to decrease. The cement mortar containing wollastonite expanded slowly but for a longer period. Therefore the long term expansion of the mortar even containing 30% wollastonite was still high. The expansion of all the specimens exceeded 0.04% at 42 days.

The expansion of the same mortars as in Fig. 8-4 with a large specimen size (3x3x11 in.) is shown in Fig. 8-5. The large specimens generally had the same expansion tendency as the small specimens. The expansion of the large specimens was delayed so that their expansion values are relatively low before 42 days compared to those of small specimens. The expansion of the large specimens started to exceed that of the small specimens at 84 and 98 days for plain cement mortar and 10% wollastonite mortar, and at about 112 days for the 20% and 30% wollastonite mortars. The 190-day expansion values of the large specimens was about 50% higher than those of the small specimens.

§ 8.4. Discussion

§ 8.4.1. Siliceous Materials

Siliceous particulates have been used as a supplementary cementing material in portland cement products to eliminate deterioration due to alkali-aggregate reaction and sulphate attack. The two major functions of the siliceous materials are:

(i) The dilution of the concentration of deleterious components in the cement such as alkali-salts and the calcium aluminate phase.

(ii) The adsorption or chemical combination of the deleterious components in the cement through the pozzolanic reaction of the siliceous materials during the cement hydration.

The siliceous materials may also assist in reducing the DEF expansion of high temperature cured Portland cement products. A preliminary test showed that a mixture of lime-siliceous material also had the capacity of adsorbing sulphate during moist-curing at high temperature. Reaction between sulphate and the components in the siliceous material may combine some sulphate. Research has shown that different siliceous materials had different effects in the reduction of expansion due to DEF. The ggbs and Class F fly ash were the most effective additives in eliminating the DEF expansion. No expansion was found in the cement mortar containing 30% ggbs or Class F fly ash, while the expansion of plain cement mortar was about 1.4% at 98 days. Natural zeolite and Class C fly ash were less effective than the ggbs and Class F fly ash. a greater than 30% addition of natural zeolite or Class C fly ash may be required to obtain no expansion of the blended cement mortar. The reason for the different effect between the siliceous materials on the expansion of cement mortar due to DEF is still not clear. Long-term expansion should be studied for optimum selection of a siliceous material for use with a DEF-suspect cement since the expansion of the mortar containing a siliceous materials appears to be much delayed.

§ 8.4.2. Microfibre Reinforcement

Microcracking plays an important role in the expansion due DEF. Control of microcracking by using wollastonite should reduce the expansion of a DEF-suspect cement mortar. During the process of DEF, the fracture characteristics of the cement mortar determine the expansion value. Cracks exist in the mortar for many reasons. Weathering (e.g. drying/re-wetting) is one of the most common sources. Once the crack

is formed, ettringite will preferentially nucleate and grow in it. Expansion develops and cracks propagate in a direction perpendicular to the expansive force. In cement paste, microcracks are surrounded by the hydrated cement matrix. According to Griffith (1921), the condition of crack propagation in one unit at the critical state is:

$$G = G_f \tag{8.1}$$

where in this case G is the fracture energy generated from delayed ettringite formation; G_f is the energy needed to initiate a fracture. The value of G_f is approximately constant and can be considered a material property. If $G < G_f$, the crack cannot propagate, that is, no expansion occurs. The crack begins to propagate and expansion occurs when $G > G_f$. The G_f of a fibre-reinforced cement mortar is much larger than that for the plain cement mortar. Therefore the expansion correspondence to crack propagation in wollastonite-reinforced cement mortar is apparently delayed and reduced. The degree of expansion reduction is proportional to the increase of wollastonite replacement for the sand.

§ 8.5. Conclusions

1. Siliceous materials including ggbs, Class F fly ash, Class C fly ash, silica fume and natural zeolite can be used in high temperature cured precast portland cement products to reduce or eliminate deleterious expansion due to DEF.
2. The ggbs and Class F fly ash are more effective mineral additives in suppressing the DEF expansion than Class C fly ash, silica fume and natural zeolite.
3. Wollastonite microfibre can be used to suppress the DEF expansion.

Chapter 9

SUMMARY, CONCLUSIONS, RECOMMENDATIONS AND SUGGESTIONS FOR FUTURE STUDY

- Mechanisms of Delayed Ettringite Formation (DEF)
- A Proposed Test Method to Determine DEF Potential of Portland Cements
- Preventive Measures to Reduce DEF-Induced Deleterious Expansion

§ 9.1. Summary

Extensive laboratory tests were carried out to investigate the mechanisms of delayed ettringite formation (DEF) in portland cement products initially moist-cured at high temperature, to develop a test method determining the DEF potential of a given portland cement and to suggest preventive measures to reduce or eliminate the deleterious expansion of portland cement products due to DEF. Fundamental research on the mechanisms of DEF are reported in Chapters 3, 4 and 5. Cracking characteristics of portland cement mortars or concretes are presented in Chapter 6. A proposed test method to determine the DEF potential of portland cements is reported in Chapter 7. Preventive measures to reduce DEF in portland cement products are in Chapter 8. A draft test method for stability of portland cement mortar initially moist-cured at high temperature for possible standardization by ASTM or CSA is provided in Appendix 1.

§ 9.1.2. Mechanisms of Delayed Ettringite Formation (DEF)

The reaction between sulphate and C_3A to form AFt occurs in portland cement upon hydration at very early ages. A short pre-storage period prevents complete consumption of sulphate. The remaining sulphate, or sulphate from decomposition of the calcium sulphoaluminate hydrates (e.g. AFt), will be rapidly adsorbed by C-S-H gel forming "phase X" in the cement product when high temperature moist-curing follows. Therefore, an internal sulphate source for DEF is formed in the cement products. The sulphate adsorbed by C-S-H gel at high temperature will be released slowly at later ages when the cement products are placed in a moist environment (e.g. out-door panels and rail-way sleepers). Pre-existing cracks can accelerate the nucleation of ettringite crystals. Nucleation of a crystal requires less surface energy in a crack than in the cement paste matrix. Pre-existing cracks can be induced by a weathering process. Out-door structures may experience thermal-drying. The surface temperature of a concrete product under

solar radiation can be higher than 80 °C in the summer. Sulphate ions, after release from the C-S-H gel, will diffuse into the nearest microcrack and react with the Al-bearing materials in the crack to nucleate and crystallize ettringite. Growth of ettringite crystals opens the crack and damages the cement products. A cement product having no pre-existing crack may also suffer deterioration due to DEF, but it requires more energy and thus longer time.

§ 9.1.3. A Proposed Test Method For Stability of Portland Cement Mortar Initially Moist-Cured at High Temperature

The test method is outlined in detail in Appendix 1. Some critical conditions and procedures of the test method are as follows:

(1) Pre-storage time

The pre-storage time is a critical parameter determining the severity of the test method. A long pre-storage time allows sulphate to completely react with C_3A forming ettringite. This reduces the amount of sulphate available for adsorption by C-S-H gel during the high temperature curing. One hour pre-storage is suggested.

(2) Curing Temperature

The curing temperature determines the expansion rate and magnitude of a portland cement product due to DEF. An increase of curing temperature (e.g. from 65 to 95) would significantly accelerate the expansion rate and enhance the final expansion value. A curing temperature of 95 °C is suggested.

(3) High Temperature Curing Period

Prolonging the high temperature curing period would increase the ultimate expansion of a portland cement product. A long period of high temperature curing enhances the decomposition of AFt or AFm phases and the degree of sulphate adsorption by C-S-H gel. The severity of this internal sulphate source for DEF is determined by the

amount of sulphate adsorbed by the C-S-H gel. A period of 12 hours high temperature curing is suggested.

(4)Thermal Drying

The thermal drying pre-treatment simulates the weathering process to create microcracks in the portland cement products after high temperature curing. This treatment is mainly a crack-making process rather than a phase-changing process. The dissolved sulphate has been adsorbed by the C-S-H gel after the high temperature curing. Further decomposition of calcium sulphoaluminate hydrates (e.g. AFm phase) may still occur, but the amount of released sulphate will be very small. Sulphate is difficult to release from the C-S-H gel during drying. One thermal drying/re-wetting cycle may be considered in a rapid test method.

(5) Sand Types

Use of a different sand will give different expansion characteristics of a portland cement mortar due to DEF. Expansion develops more rapidly in the mortar made with coarse sand than with fine sand. Mortar made with natural river sand has a higher expansion value than that made with the standard sand. River sand is not suitable for a standard test method since its characteristics are altered with different batches. A 20-30 standard (silica) sand (conforming to ASTM C 778) can be selected for a standard test providing high enough expansion in a reasonably short period.

Although the test parameters related to above critical conditions and procedures used in this proposed test method (e.g. one hour pre-storage, 14 hours moist-curing at 95°C and 24 hours drying at 85 °C) are more severe than in some precast concrete production, this test method may still be useful particularly in evaluating a cement for use in the precast concrete structures which will experience out-door weathering.

§ 9.1.4. Preventive Measures to Reduce the Deterioration of Portland Cement Products Due to DEF

Siliceous materials can be used in portland cement products to reduce or eliminate deterioration due to DEF. Different siliceous materials have different characteristics with respect to the reduction of the deleterious expansion. Ggbs and Class F fly ash are more effective in eliminating the DEF expansion than Class C fly ash, silica fume and natural zeolite. The long term expansion should be studied for the selection of a siliceous material for use with a DEF-suspect cement since the expansion of the mortar containing a siliceous material appears to be much delayed.

Control of microcracking through the use of wollastonite microfibres should reduce the expansion of a DEF-suspect cement mortar as microcracks play an important role in the expansion due to DEF. The energy needed to initiate a crack in the fibre reinforced cement mortar is much larger than in the plain cement mortar. The expansion resulting from crack propagation in wollastonite reinforced cement mortar is apparently delayed and reduced. The degree of reduction is proportional to the wollastonite content.

§ 9.2. Conclusions

Mechanisms

1 Internal Sulphate Source (phase X) forms in C-S-H - Gypsum - Water System in the temperature range from 25 to 85 °C.

2 The rate of gypsum depletion increases with the increase of curing temperature.

3 The C-S-H gel, containing sulphate adsorbed at high temperature, will release the sulphate more slowly than gel that has adsorbed sulphate at normal temperature.

4 A slower release of sulphate from an internal sulphate source is critical for DEF.

5 Nucleation of crystals in cement pastes including ettringite will preferentially occur in cracks rather than on plane solid surfaces under conditions of supersaturation.

6 Sulphate required for ettringite formation in a crack migrates from the cement matrix through the pore solution.

Accelerated Test Method

7 The proposed test method can be used to determine the expansion potential, due to DEF, of the cement mortar (made with a portland cement) initially moist-cured at high temperature.

8 The critical conditions in for an accelerated test method are a curing temperature over

90 °C, a 14-hour curing period and one hour pre-storage at ambient temperature.

9 A 20-30 standard sand conforming to ASTM C 778 is suggested for use in making mortar specimens.

10 A thermal drying pre-treatment of mortar specimens after the high temperature curing step in the proposed test accelerates the expansion due to DEF.

Preventive Measures

11 Siliceous materials including ggbs, Class F fly ash, Class C fly ash, silica fume and natural zeolite can be used in high temperature cured precast portland cement products to reduce or eliminate deleterious expansion due to DEF;

12 The ggbs and Class F fly ash are more effective mineral additives in suppressing the DEF expansion than Class C fly ash, silica fume and natural zeolite.

13 Wollastonite microfibre can be used to suppress the DEF expansion through reinforcement of the cement matrix and reduction of microcracks due to the drying/wetting treatment.

14 Wollastonite is not able to completely eliminate the deleterious expansion due to DEF.

§ 9.3. Recommendations for Preventing Concrete Deterioration due to DEF

1 Select a DEF-free cement having low blaine fineness (e.g. < 4500 cm^2/g) and SO_3 content (e.g. SO_3 < 3.5%) for the production of high temperature (> 65 °C) moist-cured concrete products.

2 Evaluate the DEF-potential of a candidate cement by an accelerated test method described in APPENDIX 1. The cement exhibiting expansion higher than 0.04% before 56 days according to the test method is not recommended for high temperature moist-cured concrete products.

3 Use ground granulated blast-furnace slag (ggbs) or Class F fly ash in a concrete mixture to replace about 30% fine aggregate (by volume), if a DEF-suspect cement has to be used. An evaluation of DEF-potential of the blend cement containing ggbs or fly ash by conducting an accelerated test (APPENDIX 1) is highly recommended.

§ 9.4. Suggestions for Further Study

1 Study the stability of cements having controlled compositions, e.g. alkali content, sulphate content, C_3A content.

2 Investigate a large suite of cements from different plants and production periods.

3 Study the stability of cements having different fineness values.

4 Case studies of actual concrete pavements and structures made with Type 30 portland cement would be instructive. (e.g. pavement deterioration found in Iowa highways.)

APPENDIX 1

PROPOSED TEST METHOD FOR DETERMINING THE STABILITY OF PORTLAND CEMENT MORTARS MOIST-CURED AT HIGH TEMPERATURE

A proposed test method prepared for standardization by ASTM or CSA

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1. Scope

1.1 This test method covers the determination of the expansion of mortar bars made from portland cement and initially moist-cured at high temperature. This test method applies only to portland cements.

1.2 The values stated in inch-pound units are to be regarded as the standard.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards*:

C 109 Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or 50-mm Cube Specimens)

C 305 Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency

C 490 Specification for Apparatus for Use in Measurement of Length Change of Hardened Cement Paste, Mortar, and Concrete

C 511 Specification for Moist Cabinets, Moist Rooms and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes

C 788 Specification for Standard Sand

C 1005 Specification for Weights and Weighing Devices for Use in the Physical Testing of Hydraulic Cements

C 1038 Test Method for Expansion of Portland Cement Mortar Bars Stored in Water

D 1193 Specification for Reagent Water

3. Significance and Use

3.1 This test method, when applied to portland cement products initially moist-cured at high temperature, determines the amount of expansion of a mortar bar when it is stored in lime-water. The amount of mortar bar expansion is related to cement composition and fineness.

3.2 This test method is particularly useful for predicting the stability of precast portland cement product which will experience severe our-door weathering in service. Stability is predicted if the cement used has not exceeded the expansion limit determined by ASTM Test Method C 1038 and no reactive aggregate is used.

3.3 The results of tests performed using this method furnish information on the likelihood that a precast product made with the test cement will experience deleterious expansion due to delayed ettringite formation.

3.4 Criteria to determine the potential for deleterious expansion has not been finally confirmed. (It appears that a cement may be considered to be deleterious if the expansion from this method exceeds 0.04% at 42 days or 0.10% at 56 days.)

3.5 A cement for use in products initially moist-cured at high temperature may be selected by requiring that the amount of expansion in lime-water does not exceed a recommended limit.

3.6 Additional studies may be appropriate to develop information on the potential expansion of the cement in combination with a mineral admixture, when it has been concluded from the results of this test method that the cement should be considered potentially deleterious.

4. Apparatus

4.1 *Weights and Weighing Devices*, conforming to the requirements of ASTM Specification C1005. The weighing device shall be evaluated for precision and accuracy at a total load of 2 kg.

4.2 *Glass Graduates, Molds, and Length Comparator*, conforming to the requirements of Specification C 490.

4.3 *Moist Cabinet or Room*, conforming to the requirements of ASTM Specification C 511.

4.4 *Mixer, Bowl, and Paddle*, conforming to the requirement of ASTM Method C 305.

4.5 *Trowel and Tamper*, conforming to the requirements of Test Method C 109.

4.6 *Oven* - A convection oven with temperature control maintaining 185±3°F (85±1.7°C).

4.7 *High temperature Moist Cabinet* - The cabinet shall be temperature controlled over the range from room temperature to 203°C (95°C). The capacity of the heating unit shall be such that with maximum load (water plus specimens) the temperature in the cabinet may be raised to 203°F (95°C) in 45 to 75 min from the time the heat is turned on. The cabinet shall be capable of maintaining a relative humidity of 100% at the saturation pressure corresponding to the test temperature.

5. Temperature and Humidity

5.1 *Preparation Room, Dry Materials, and Mixing Water*- The temperature of the preparation room, dry materials, and mixing water shall be maintained between 68 and 81.5 °F (20 and 27.5 °C) and the relative humidity of the preparation room shall not be less than 50%.

6. Reagents and Materials

6.1 *Mixing Water* - Potable water is satisfactory for routine tests. Reagent water conforming to Type III B of ASTM Specification D 1193 shall be used for all co-operative tests in case of dispute.

6.2 *20-30 Standard Sand* - The 20-30 standard sand for making the test specimens shall be natural silica sand conforming to the requirements for 20-30 standard sand in ASTM Specification C 778. The 20-30 standard sand shall be graded as follows:

Sieve	Percentage Passing
1.18-mm (No.16)	100
850-μm (No.20)	85 to 100
600-μm (No.30)	0 to 5

7. Procedure

7.1 *Number and Dimensions of Test Specimens* - Make four 1x1x11 1/4-in. (25x25x285-mm) test specimens for each cement.

Note 1 - In routine tests, 1x1x6-in. (25x25x160-mm) specimens may be used; in case of dispute, results obtained with 1x1x11 1/4-in. (25x25x285-mm) specimens shall govern.

7.2 *Specimen Molds* - Prepare the specimen molds in accordance with the requirements of ASTM Specification C 490. In addition the interior surfaces of the mould shall be covered with a release agent. A release agent will be acceptable if it serves as a parting agent without affecting the setting of the cement and without leaving any residue which will inhibit the penetration of water into the specimen.

Note 2 - TFE-fluorocarbon tape complies with the requirements for a mold release agent.

7.3 *Proportioning, Consistency, and Mixing of Mortar*:

7.3.1 The quantities of dry materials required to prepare four 1x1x11 1/4-in. (25x25x285-mm) specimens are 500 g of cement and 1375 g of 20-30 standard sand. The amount of mixing water is 240 mL for non-air-entraining portland cements.

7.3.2 Mix the mortar in accordance with the procedure described in ASTM Method C 305.

7.4 *Molding Test Specimens* - Immediately upon completion of mixing, remove the paddle and the bowl from the mixer and shake the excess mortar from the paddle into the bowl. Fill the mold in two layers, compacting each layer with the tamper. Work the mortar into the corners, around the gage studs, and along the surfaces of the mold with the tamper until a homogeneous specimen is obtained. Level the mortar off flush with the top of the mold after the top layer has been compacted. Smooth the surface with a few strokes of the trowel.

8. Storage, High Temperature Moist Curing and Thermal Drying of Test Specimens

8.1 *Prestorage* - Place the test specimens in the moist cabinet or moist room at 23 °C. Keep all test specimens in the molds in the moist cabinet or moist room for 1h with the upper surfaces exposed to the moist air but protected from dripping water.

8.2 *High Temperature Moist Curing* - Store the test specimens in the high temperature moist cabinet after pre-storage. Turn on the heating unit to allow the temperature to rise to 203±3°F (95±1.7°C) in 60 min. Maintain the test specimens at 203±3°F (95±1.7°C) for 12h. Turn off the heating unit and cool the test specimens for 4h. Remove the specimens from the molds, properly identify, and place in water maintained at 73.4±3°F (23.0±1.7°C) for 6h prior to making the initial length measurement. The relative humidity in the cabinet shall be maintained at 100%.

8.3 *Thermal Drying* - Place the test specimens in an oven with the temperature maintained at 185±3°F (85±1.7°C) for 24h after the initial length measurement. Cool the test specimens to room temperature.

8.4 *Subsequent Storage* - Store the test specimens after thermal drying in saturated lime water in a tank in the moist cabinet or moist room. The specimens shall be covered with at least 1/4in. (6.4 mm) of water during storage. Keep the storage water clean by changing it as necessary.

9. Length Measurements

9.1 Remove the specimens from water storage, one at a time, and wipe with a damp cloth before measuring. Measure the specimens for length by means of the length comparator.

9.2 The initial reading on test specimens is made prior to thermally drying at the age of 24h±15min from the time the cement and water are mixed together. Measure the specimen length subsequently at the age of 42 and 56 days.

9.3 Additional information of value may be obtained by returning the specimen to water storage and making additional length measurements at ages earlier and later than 56 days. Measurements at ages 3, 6 and 12 months and, if necessary, at least every 3 months thereafter are suggested.

10. Calculation

10.1 Calculate the difference in length of the specimen at 24h, 42 days 56 days and additional ages from casting to the nearest 0.001% of the effective gage length and report as the expansion of the specimen at that time. Report the average of the three specimens to the nearest 0.01% as the expansion for a given period.

11. Report

11.1 Report the following information:

11.1.1 Type and source of portland cement,

11.1.2 Record of pre-storage time and curing temperature,

11.1.3 Average length change in percent for each reading of the specimens,

11.1.4 A graph of the length change data from the time of the initial reading to the time of the report.

12. Precision and Bias

12.1 *Precision* - The precision of this test method has not been determined.

12.2 *Bias* - Since there is no accepted reference material suitable for determining the bias for this test method, no statement on bias is made.

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