

# **A kinetic model for prediction of cement susceptibility to delayed ettringite formation in concrete, Part 1: Theoretical model concept**

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## **Abstract**

A model is proposed for predicting the intrinsic potential of Portland cements to exhibit delayed ettringite formation, when used in cementitious systems. The model has been developed on the basis of kinetic reaction theory and consists of a set of two equations which define the primary conditional requirements on cement chemistry. The important conditions, sufficient alumina content exceeding a certain unknown threshold and  $SO_3/Al_2O_3$  ratio high enough to promulgate ettringite infilling pressures over and above counter microstructural factors, are mathematically expressed. Both conditions have been reported in the literature by various authors basing on experimental observations.

The proposed model can be a useful screening tool for rapid evaluation of cements against their proneness to delayed ettringite formation (DEF) and may be applied in cement manufacture, import depots, ready-mix plants, and many others or for selection of cements for specific applications. Due to the intrinsic nature of the model, it has the potential to reveal the underlying expansive behaviour that may be suppressed or not easily observed from experimental tests alone. Validation of the model against experimental data from literature has been undertaken in Part 2 of this work.

## **Introduction**

Construction practice demands faster strength development, which allows for more optimal and cost-effective use of equipment, such as quicker stripping of formwork. One of the methods commonly used in the concrete industry to attain significantly high early strengths is heat-curing [1]. Heat treatment or steam-curing is effective through its increase of the hydration rate, speed up the attainment of higher strengths to allow for early demoulding or, in the case of concrete members to be prestressed, to make possible the earliest possible stressing of concrete, hence boosting the rate of utilization of production equipment [1,2]. In addition, this technique has the advantage of reducing creep, shrinkage and loss of prestress in concrete [1].

Heat curing helps to develop high early strengths and thus allows for some savings to be made in the economics of equipment. Yet, curing at elevated temperatures does not just come with advantages: it brings about setbacks as well. This accelerated curing technique drawbacks are both of structural aspect, as well as of durability issue. Heat-curing of concrete brings about a pathology specific to heat-treated concrete commonly referred to as delayed ettringite formation,

a form of internal sulphate attack. Numerous factors have been identified as conducive to DEF-related expansive damage. Among these factors are the curing temperature, cement chemical composition, availability of moisture during storage or service of the structure, and heat-treatment duration. Also, factors pertaining to the mix design such as water-cement ratio, aggregates properties, and the pre-curing setting time have been cited for their influence on expansion due to DEF. Other factors, though not being the direct causes for DEF, have been reported to exacerbate it. These include the presence of micro-cracks, co-presence of alkali-silica reaction, the presence of large quantities of magnesium sulphate in the cementitious system.

Durability of concrete is an issue of paramount importance, as it determines the service life of the product. Concrete longevity may be limited by many factors, being physical, chemical, or structural causes. A concrete structure's life can get shortened when overloaded, with the rise of cracking within the structure ultimately leading to accelerated degradation and failure. Shortening of the life of the structure can also occur as a result of physical actions such as successive freeze-thaw, cavitation, among others. Chemical actions that can lead to concrete deterioration may be caused by ingress of carbon dioxide, chloride, sulphate, or soft water. Understanding the mechanisms that pertain to the deterioration of concretes, and being able to model these deterioration processes is a step forward towards the prediction of service life of concrete structures.

The present study is concerned with the modelling of sulphate attack of concretes; and is particularly limited to internal sulphate attack associated with DEF.

### **Literature Review on modelling of sulphate attack in concrete**

Different approaches have been used in the modelling of concretes deterioration mechanisms including sulphate attack. Some of the approaches that have been used are mathematically based, while others are founded on mechanics, physics, chemistry, or a combination of two or more of these scientific fields. Basista and Weglewski [3,4] proposed a micromechanical model to predict external sulphate attack based on a topochemical reaction mechanism in which a reaction term coupled with Fick's second law are considered to govern the transport properties of sulphate ions. Transport properties are taken to degrade with the evolution of formation of expanding ettringite crystals in the micro-cracked hardened cementitious system.

Tixier [5] and other authors [6, 7] applied cement chemistry, physics aspects and theories of fracture mechanics of concrete to develop a model for prediction of degradation of cement-based materials exposed to external sulphate attack. They based their model on a diffusion-reaction mechanism, and accounted for sulphate penetration, reaction, damage evolution, and expansion.

As regards DEF-related internal sulphate attack, attempts have been made since the late eighties to determine necessary conditions that are conducive to this kind of expansive damage. Most of the work available in the literature is based on empirical observations deduced from experimental data. And, to the knowledge of the authors of this paper, no successful attempt has been made to numerically model DEF-related expansion based on a scientific theory.

While general understanding was developed quickly as to the curing conditions that lead to DEF, especially heat-treatment of specimen beyond 70°C and applying short or no pre-curing time, Heinz and Ludwig [8] were among the earliest to place limiting values on cement composition favoring the appearance of expansion in heat-cured mortars. They suggested that for DEF expansive damage to arise, it was necessary that the sulphate to aluminates (total) ratio of the cement used be 0.5 or higher. Later, Heinz, Ludwig, and Rudiger [9], re-affirmed that expansion was dependent strongly on cement composition, mainly influenced by the  $\frac{SO_3}{Al_2O_3}$  ratio. But they also noted that while considering this ratio, the sulphate content carried more influential weighting than the alumina. So they proposed a modified version of the ratio, in form of  $\frac{(SO_3)^2}{C_3A}$ , where  $C_3A$  represents the active alumina. In the latter expression, values less than 2 are required to avoid occurrence of DEF expansion. The authors [8,9] suggested that there was a need for alumina content to exceed a threshold value in order for expansion to be possible. They noted that sulphate resistant cements, which are known to have low  $C_3A$  contents, do not exhibit DEF expansion even though sulphate contents were increased to such degrees that the ratio  $\frac{SO_3}{C_3A}$  reached prohibitively high values.

In later studies, Lawrence [10] reported positive correlations between  $Na_2O$ ,  $SO_3$ ,  $CaO$ , and  $MgO$ , and expansion whilst  $C_3A$  was shown to be negatively influential on expansion. Basing on correlation coefficients, he suggested an expression (1) supposedly for predicting DEF expansion. The expression was determined from expansion test results at 800 days.

$$\text{Expansion}_{800} (\%) = 9.51 + 0.304 \cdot SO_3 + 0.00085 \cdot \text{fineness} + 1.728 \cdot \text{combined } Na_2O - 0.162 \cdot CaO - 0.040 \cdot C_3A \quad (1)$$

Also, threshold values of 0.83%, 0.22%, 3.6%, 1.6% for  $Na_2O_{eq}$ ,  $Na_2O$ ,  $SO_3$ , and  $MgO$  respectively were suggested by Taylor [11], for which at least two or three should be exceeded for a great chance of damaging expansion beyond 0.2% to occur. Kelham [12] later reported a relationship (equation 2) between cement fineness,  $MgO$ ,  $C_3A$ ,  $C_3S$ ,  $SO_3$ , and  $Na_2O_{eq}$ , and expansions of mature specimens heat-cured at 90°C for 12 hours.

$$\text{Expansion} (\%) = 0.00474 \cdot \text{specific surface area} + 0.0768 \cdot MgO + 0.217 \cdot C_3A + 0.0942 \cdot C_3S + 1.27 \cdot Na_2O_{eq} - 0.737 \cdot ABS [SO_3] - 3.7 - 1.02 \cdot Na_2O_{eq} - 10.1 \quad (2)$$

From Kelham's expression, there appears to exist a pessimum sulphate content at about 4% at which expansion is maximal. The pessimum sulphate value together with the degree of expansion increase when cement alkali content increases as seen figure 1. The existence of a pessimum value of sulphate to alumina ratio of the cement was earlier reported by Lewis [13].

Further still, Grattan-Bellew and Beaudoin [14] showed the existence of a pessimum value for  $C_3A$  on DEF. In their study, high alumina contents were examined by means of microanalysis of the inner CSH product of heat-treatment mixtures containing slag. Slag is known to contain quite significant amounts of alumina. Lewis [13] suggested that the low values of  $\frac{SO_3}{C_3A}$  ratio obtained in the slag incorporated mixes may be responsible for the effectiveness of slag in mitigating expansion due to DEF. The low sulphate to alumina ratios would favour the formation of monosulphate rather than ettringite.

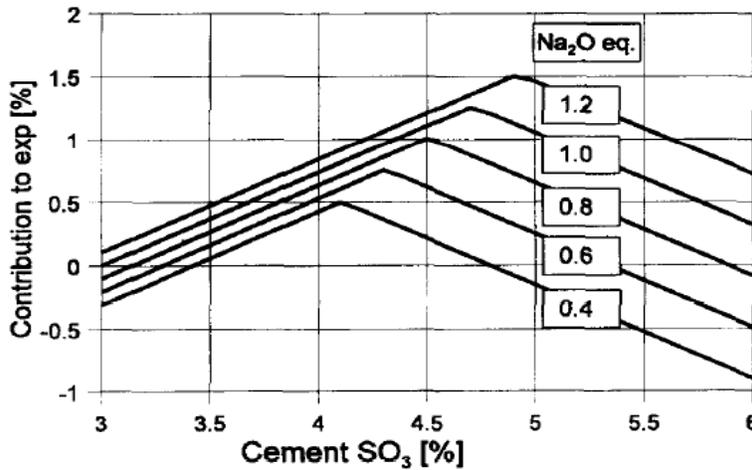


Figure 1: Pessim effect of sulphate on expansion for different alkali contents [12]

Zhang et al [15] also proposed an expression they named DEF index (3), representing expansion values for cement mortars and concretes heat-cured at 85°C for 12 hours.

$$\text{DEF index} = \left(\frac{SO_3}{C_3A}\right)_{molar} \times \frac{(SO_3 + C_3A)_{weight\%}}{10} \times \sqrt{Na_2O_{eq(weight\%)}} \quad (3)$$

This formula was determined through trial and error as well as from basic understanding of the influence of cement composition on delayed ettringite formation. The expression also indicates that DEF is dependent not only on sulphate to aluminate ratio, but also on the individual sulphate and alumina contents as these will determine the amount of ettringite formed, together with the combined alkali content.

It has to be noted that the equations (1-3) are only valid for specific sets of cement compositions and expansion data. The expressions are not of much use when applied to many other sets of data [16]. Clearly, while a great deal of understanding has been attained regarding the effect of different compositional chemical parameters on DEF expansion, there remain several contradictions in results. This suggests that DEF-related expansion does depend not only on chemical composition of cement used, but on other factors as well. In an effort to develop a holistically model of DEF-related expansion, Taylor [17] undertook a study aimed at providing some understanding of DEF-related expansion based on three kinds of actions which he suggested are equally influential on expansion:

- Chemistry, as it determines the amount of ettringite (the source of expansion) formed
- Paste microstructure, as it governs the stresses resulting from ettringite formation
- Concrete microstructure, as it controls the response of the materials to stresses arising from ettringite formation

Concerning the effect of cement chemistry, especially the two components that make ettringite i.e. sulphate and aluminate, Taylor showed that various pessima are possible: for a given content of sulphate, lack of alumina will lead to no ettringite formed, and an excess of alumina will yield no ettringite as well since the latter case will favour the formation of monosulphate rather than ettringite. Also, for a given amount of aluminate in the cement used, absence of sulphate will yield no ettringite, while excess sulphate will result in ettringite remaining in the system even after heat curing. This occurs since ettringite stability increases with higher concentration of sulphate ions in the medium.

### **Proposed Model**

The objective of the present work is to predict the susceptibility of Portland cements based solely on parameters of primary influence such as the chemical composition and cement fineness. In this work, consideration is given to the most important components in the formation of ettringite, that is, sulphate and alumina. In addition, effects of silica, ferrite, and magnesia are also considered. Expansion due to sulphate attack is the consequence of ettringite formation causing volumetric increase in hardened cementitious system. While this work is not focussed on the expansion mechanism or process, it is based on the understanding that the amount of ettringite formed at later stages upon wet storage of heat-treated specimen will first fill up some available free space (of capillary pores) to a certain extent before the excess ettringite initiates observable expansion.

Accordingly, this work will be conducted in such a manner as to determine positive formation of ettringite under the conditions of heat-treated medium. After heat curing, there are micro-structural and compositional changes that occur in the specimen, rendering it susceptible to late formation of ettringite. Depending on cement composition used, the changes induced by heat-curing may be such that the final chemical aspect of the specimen can be of the nature that may or may not promote the formation of ettringite. And where the chemical aspect of the specimen can promote formation of ettringite, it is possible that the amount formed may not be sufficient to cause expansion. So, to determine if a particular cement will be susceptible to DEF damage, one should first estimate its possible composition following heat treatment, and from there assess its ability to form ettringite. Finally, an evaluation of the quantity of ettringite formed is done to determine if its amount can be sufficiently large so as to exceed the available space of capillary pores thus resulting in expansion.

Upon heat treatment of a cementitious mixture, a number of various chemical reactions occur, namely the formation of ettringite and its decomposition into its basic constitutive ions of sulphate and alumina, some of which get adsorbed onto CSH gel while others are transformed into monosulphate and hydrogarnet. Upon later storage in a moist environment, the aluminate that has combined with the silica gel is no longer available for participation in the formation of ettringite. It has been suggested that some of this alumina substitutes for silica in the CSH gel structure, and remains there even upon specimen storage under water [17] while another portion of alumina will be bound as hydrogarnet and does not possess any reacting capabilities [18]. Only monosulphate and sulphate are capable of reacting to form ettringite. The rate of ettringite formation as well as the amount of ettringite formed depends upon the concentration of monosulphate and sulphate available. The amount of monosulphate and sulphate available for reaction after heat treatment depends mainly on the composition of cement used and other factors such as the duration and temperature of curing, among others.

### **Basis for the Test**

It has been shown that there is no direct relationship between the amount of ettringite generated and the degree of expansion [19]. However, Taylor [17] pointed out that precaution should be exercised when assessing data related to quantitative determinations of ettringite by thermal analysis methods or XRD, since the techniques may not be adequate enough to accurately account for the small and possibly imperfect ettringite crystals responsible for expansion. Generally, however, examination of expansion results reported by Odler and Caulan-Subauste [20], suggests that the greater the amount of ettringite formed, the higher the expansion recorded.

Furthermore, whatever the mechanism of expansion through which expansion occurs as a result of ettringite formation, there are indications that the higher the likelihood of ettringite formation there is, the bigger the chance for expansion related to delayed ettringite formation there will be. Factors increasing the probability of formation of ettringite are, amongst others, higher concentrations of reacting substances that are tricalcium aluminate, sulphates, and calcium hydroxide, as well as high sulphate to aluminate ratios.

Concluding from the ettringite crystallisation pressure formula they developed, Ping and Beaudoin [21] stated that the formation of larger amounts of ettringite is not a requirement for increased expansions, since expansions result from pressure generated as a consequence of increased reactants activities in the aqueous system, as shown in equation (4). Yet, any increase in reactant concentrations, which is likely to lead to large amounts of ettringite formed, will also increase reactants activities in the liquid phase, thus leading to increases in generated pressures and expansions. This could be the reason why higher expansions are observed in a lime-containing system rather than in lime-free ones, as in the former greater activities of calcium ions are guaranteed with the supply from the solid lime [21].

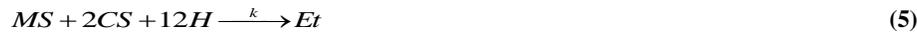
$$P_c \approx \frac{RT}{V_s} \ln A \quad (4)$$

Where,  $P_c$  represents the pressure generated as a result of ettringite nucleation and crystallisation from pore solution;  $R$ ,  $T$ ,  $V_s$  are the ideal gas constant, temperature in Kelvin, and the molar volume of ettringite respectively, while  $A$  represents the activities of reacting substances in the pore solution.

Based on the swelling-based expansion theory suggested by Mehta [22], which states that expansion is a consequence of water uptake by colloidal amorphous ettringite particles that have been formed from a through-solution reaction mechanism, the more the amount of ettringite colloids formed, the higher will be their final total volume after water uptake, provided that sufficient quantities of water is available. Thus, any efforts to predict the susceptibility of a particular cementitious system to DEF-related expansion should not be done without taking into account factors affecting the probability, and the extent of ettringite formation, the chemical composition of the cement being one of them. Chemical reaction kinetics can be applied to to derive the amount of ettringite formed.

### Reaction Kinetics

DEF occurs as a result of a reaction in which monosulphate combines with sulphates as in equation (5):



Kinetics theories stipulate that the reaction above can be studied through its rate, which is either considered in terms of the production of the product ( $R_e$ ), or in terms of the destruction of the reacting substances ( $R_m$  or  $R_s$ ). The reaction rate (destruction rate of a reactant or the production rate of a product) as stated by the 'Law of Mass Action' [23, 24] is proportional to the product of reactants concentrations each raised to a power equal to its respective partial order.

$$R_e = \frac{d[Et]}{dt} = k[MS]^a [CS]^b \quad (6)$$

$$R_m = \frac{d[MS]}{dt} = -k[MS]^a [CS]^b \quad (7)$$

$$R_s = \frac{d[CS]}{dt} = -2k[MS]^a [CS]^b \quad (8)$$

**K** is the reaction rate constant, while **a** and **b** are partial orders of the reaction in respect to monosulphate and sulphate respectively.

A number of researchers [3-7] have previously modelled sulphate attack with some satisfactory degree of accuracy, using unity as partial orders of reaction between aluminates (simply calcium aluminates or calcium aluminate monosulphates) and sulphate. Considering those orders as given, the solution to the above reaction rate equation gives:

$$\frac{1}{[CS]_o - 2[MS]_o} \left( \ln \frac{[CS]}{[MS]} - \ln \frac{[CS]_o}{[MS]_o} \right) = kt \quad (9)$$

The concentration of ettringite as a function of time will then be found as:

$$[Et] = [Et]_o + x \quad (10)$$

Where  $[Et]_o$  are the initial concentration values of ettringite in the medium and **x** is the solution from the equation (11) below:

$$\frac{1}{[CS]_o - 2[MS]_o} \left( \ln \frac{[CS]_o - 2x}{[MS]_o - x} - \ln \frac{[CS]_o}{[MS]_o} \right) = kt \quad (11)$$

Concentrations of reacting monosulphate and sulphate ( $[MS]_o$  and  $[Et]_o$  being their respective initial values in the reaction medium) respectively are given by:

$$[MS] = [MS]_o - x \quad (12)$$

$$[CS] = [CS]_o - 2x \quad (13)$$

Graphically, the solution may be plotted as in figures 1, 2, and 3, for  $[MS]_o = 0.2$  mole/litre,  $[CS]_o = 0.2$  mole/litre,  $[Et]_o = 0$  mole/litre, and  $k = 7.2 \times 10^{-8}$ .

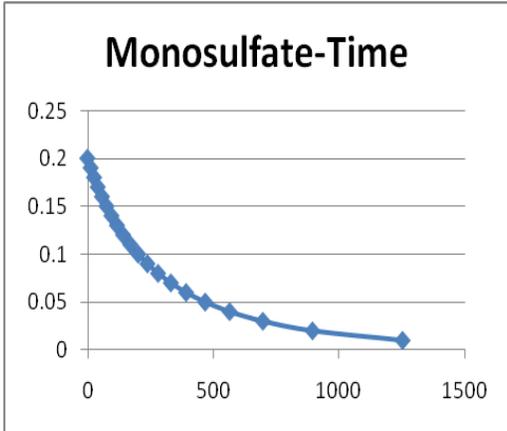


Figure 2: Plot of monosulfate concentration versus time

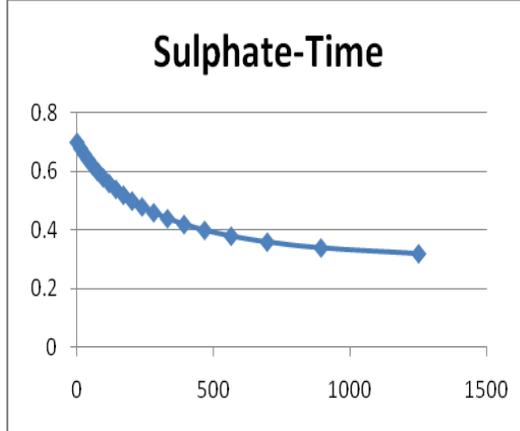


Figure 3: Plot of sulphate concentration versus time

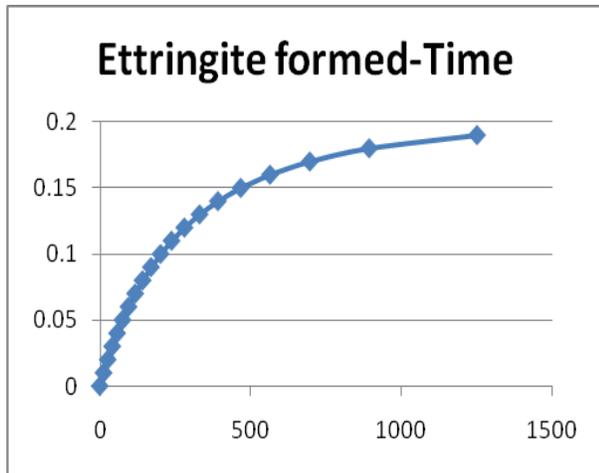


Figure 4: Plot of ettringite concentration versus time

### Test Formula Development

The overall objective of the model test is to provide a measure of the susceptibility of a specific cement to DEF-related expansive damage, basing solely on cement characteristics of chemical composition and specific surface area.

It is generally established that DEF damage is a consequence of at least three factors:

- High curing temperatures (beyond 70°C)
- Availability of moisture after concrete has already hardened
- And the right cement compositional characteristics

In our present exercise, it can be assumed that both of the first two conditions are met, the only factor remaining being the characteristics of cement. Expansion ensues from ettringite formation, as discussed in the preceding sections.

From the work of various authors [3-7], the amount of ettringite formed needs to exceed the maximum that can be accommodated within the specimen capillary pores for expansion to occur. Thus, one can define a maximum volume of formed ettringite that can be accommodated in capillary pores,  $V_o$  that should first be filled before expansion can start occurring.

$$V_o = f\Phi \quad (14)$$

$f$  being a shift parameter that depends on how much of the capillary pores volume is available to accommodate the in-filling formed ettringite, and  $\Phi$  being the capillary porosity of the specimen.

In normally hydrated mortars, capillary porosity  $\Phi$  can be estimated from equation (15) [ref. 5]:

$$\Phi = \max\left(f_c \frac{c}{\frac{w}{c} + 0.32} - 0.39\alpha, 0\right) \quad (15)$$

However, heat-curing induces microstructural changes visible in such factors as the increase in final capillary porosity and permeability. Thus, there is a need for another route to be used for the numerical estimation of  $\Phi$ .

The relative volumetric expansion resulting from ettringite formation is dependent upon the amount of ettringite formed, as is shown in equation (16):

$$\frac{\Delta V}{V_o} = \frac{V_f - V_o}{V_o} \quad (16)$$

Where,  $V_f$  is the volume of the specimen at a specific moment of time,  $V_o$  its initial volume, and  $\Delta V$  the change in volume.

Both the initial and final volumes of the specimen are made up of volume-changing substances and non-changing ones. Amongst the volume-changing components are the reactants and products partaking in the formation of ettringite i.e. monosulphate, gypsum, and ettringite, while the other ingredients i.e. aggregates and other cement paste components that are not participating in the deterioration chemical reaction of the mix are non-volume changing materials.

$$\frac{\Delta V}{V_o} = \frac{(V_{fChanging} + V_{fUnchanging}) - (V_{oChanging} + V_{oUnchanging})}{V_o} \quad (17)$$

Considering that the relative volumetric expansion resulting from ettringite formation is dependent upon the amount of ettringite formed, the volume change will be the difference between the final volume of the volume-changing ingredients and their initial volume. This leads to the expressions:

$$\frac{\Delta V}{V_o} = \frac{V_{fChanging} - V_{oChanging}}{V_o} \quad (18)$$

$$V_{fChanging} = M_{vEt} * [Et] + M_{vMS} * [MS] + M_{vCS} * [CS] \quad (19)$$

and

$$V_{oChanging} = M_{vEt} * [Et]_o + M_{vMS} * [MS]_o + M_{vCS} * [CS]_o \quad (20)$$

Where  $M_{vEt}$ ,  $M_{vMS}$ ,  $M_{vCS}$  are .....

From the equations (11-13)

We obtain:

$$\frac{\Delta V}{V_o} = \frac{M_{vEt} * x - M_{vMS} * x - 2 * M_{vMS} * x}{V_o} \quad (21)$$

$$\frac{\Delta V}{V_o} = \frac{x(M_{vEt} - M_{vMS} - 2M_{vMS})}{V_o} \quad (22)$$

The value  $x$  being expressed in concentration units, moles of ettringite formed per litre of specimen. The reference volume  $V_o$  should be taken as a unit volume ( $V_o = 1$  litre), the molar volumes being 0.725 l per mole of ettringite, 0.310 litre per mole of monosulphate, and 0.074 litre per mole of gypsum [25]. The relative volumetric increase will be

$$\frac{\Delta V}{V} = 0.267.x \text{ per litre of specimen} \quad (23)$$

This means for each  $x$  mole of ettringite formed, the volumetric increase will be 0.267x % of the initial volume.

Expansion initiates when  $\frac{\Delta V}{V_o} > f\Phi$  (24)

That is,  $0.267 x > f\phi$  (25)

From equation (25), it is possible to estimate the amount of formed ettringite that is needed to cause observable expansion:

$$x > \frac{f\Phi}{0.267} \quad (26)$$

And the minimal amount (per litre of specimen) of ettringite formed beyond which there is expansion would be:

$$x_{Min} = \frac{f\Phi}{0.267}$$

$$x_{Min} = 3.745 f\Phi$$

Going back to equations (12-13) that describe the kinetics of delayed ettringite formation, it can be seen that the reaction stops at exhaustion of any of the reacting substances (monosulphate or gypsum). That is, the rate of formation of ettringite becomes zero when any of the concentration of the reactants is exhausted, becoming zero:

$$[MS] = [MS]_o - x = 0 \quad (27)$$

$$\text{Or } [CS] = [CS]_o - 2x = 0 \quad (28)$$

Meaning that at the stop of ettringite formation, either

$$[MS]_o = x \quad (29)$$

$$\text{Or } [CS] = 2x \quad (30)$$

The condition for the reaction to stop after enough ettringite has been made that can lead to net expansion is that both initial concentrations of monosulphate and gypsum are each enough to allow for the making of ettringite in a quantity  $x$  exceeding  $x_{Min}$

This condition can be expressed as:

$$[MS]_o > x_{Min} \quad (31)$$

$$[CS] = 2x_{Min} \quad (32)$$

The next step in the development of the test formula is now to relate the concentrations  $[MS]_o$  and  $[CS]_o$  of available sulphate and monosulphate after heat-treatment to the characteristics of cement used.

In the above, we considered the case where all aluminates in cement avail themselves for reaction into monosulphate during heat-treatment, and that all ettringite that may have formed during curing is destroyed by the end heat-curing.

Thus, one could consider writing sample contents in aluminate monosulphate and calcium sulphate as follows:

$$[MS]_o = A_c \tag{33}$$

$$[CS]_o = S_c - A_c \tag{34}$$

Where  $A_c$  and  $S_c$  are .....

However, when a grain of tricalcium aluminate is attacked by molecules of calcium sulphate, many possibilities are available as outcomes of that encounter.

There can be complete formation of monosulphate at the expense of the aluminate grain (which is very unlikely). There could as well be partial formation of monosulphate with residual aluminate staying untouched in the inner part of the grain. In this case, only a portion of this aluminate could be available for further hydration or participation into deleterious reactions, since it has been shown that dense shells form around cement grains during heat-treatment, impeding further water penetration towards the unreacted inner core of cement grains. Consequently, the degree of hydration and the ultimate strength is reduced. Also, some aluminate may have been converted into monosulphate, another portion into ettringite. Although it is accepted that ettringite that has initially been formed during the early ages of hydration is destroyed upon heat-curing, it is just as well known that in circumstances of high sulphate concentrations in the pore solution, ettringite may resist high temperature destruction. Another portion of aluminate may have entered the CSH structure, where it is known to have substituted for silica, solidly bound in the structure and having no possibilities to get freed at later stage to participate in ettringite forming reaction [17]. Another portion, the last one, of initial aluminate present in the cement, may have hydrated into hydrogarnet (upon heat treatment) which has been reported to have no noticeable reactive capabilities [18].

In a nutshell, substantial amounts of aluminate present in the cement used will be “lost” or transformed into non-reactive forms following heat curing, leaving only some considerably reduced proportion available for further reactions. The proportion of this still reactive alumina (left after heat curing) to the total alumina content in the cement could be defined by the parameter  $m$ .

As for sulphate, only some portion would be lost from early formed ettringite that is not destroyed during heat-treatment. The remaining sulphate is either in the pore solution or adsorbed, just loosely incorporated into the CSH structure, with all the prospects and capabilities of getting released later upon storage in moisture. It has been suggested [ref?] that at the end of heat-curing, there is more sulphate adsorbed in the CSH-gel than there is available in the pore solution. From the initial sulphate content in cement, only the portion that went into non-destroyed ettringite is no more available for further participation into ettringite making reactions after heat-treatment. The proportion of available sulphate to the initial sulphate content could then be named as  $n$ .

$$m = \frac{\text{TotalAluminate} - (\text{EttringiteAluminate} + \text{SilicateSubstitutedAluminate} + \text{HydrogarnetAluminate})}{\text{TotalAluminate}} \quad (35)$$

$$n = \frac{\text{TotalSulphate} - \text{Ettringite Sulphate}}{\text{TotalSulphate}} \quad (36)$$

The values of  $m$  and  $n$  can take any value between 0 and 1 but the actual values depend upon several factors including casting and heat-treatment conditions i.e. temperature, duration, materials mixing; materials parameters such as cement grains size, among others. Thus, a more general and accurate expression of expected initial concentrations of monosulphate and sulphate after heat-treatment can be written as:

$$[MS]_o = mA_c \quad (37)$$

$$[CS]_o = nS_c - mA_c \quad (38)$$

And the initial rate of ettringite formation can be written as:

$$\mathfrak{R}_{ei} = k(mA_c)(nS_c - mA_c) \quad (39)$$

When considering the effect of cement aluminates content on the initial rate of formation of ettringite, for a specific value of sulphate content, the latter (initial rate) would be varying as follows:

$$\frac{d\mathfrak{R}_{ei}}{dA_c} = k(nS_c - 2mA_c)m \quad (40)$$

The maximum value of the function for initial reaction rate or cement alumina content can be found as

$$\frac{d\mathfrak{R}_{ei}}{dA_c} = 0 \quad (41)$$

Giving then

$$A_c = \frac{n}{2m} S_c \quad (42)$$

Figure 6 represents this trend.

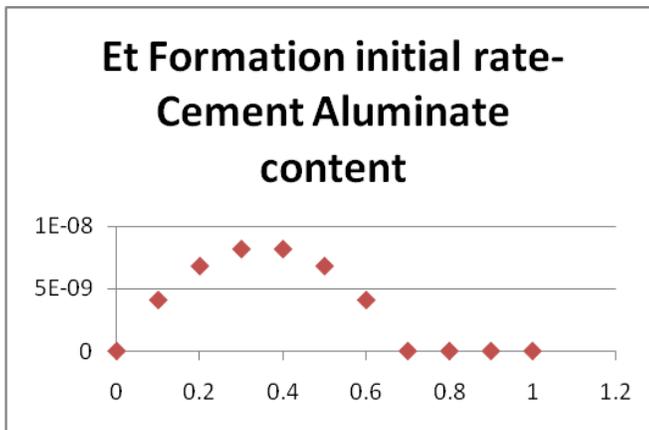


Figure 5: Ettringite formation initial rate versus cement aluminate content (for a 0.7 mole/litre cement sulphate content, and  $n = m = 1$ )

As for the case where aluminates content is known, the effect of sulphate content on the initial reaction rate would be seen through the equation (43):

$$\frac{dR_{ei}}{dA_c} = kmA_c \quad (43)$$

This expression does not yield any maximum but because it is positive, the initial reaction rate and thus the amount of expansion, will continue to increase as long as the cement sulphate content is being increased. This scenario does not account for the possibility of some ettringite remaining non-destroyed upon heat-treatment when high sulphate concentrations are present in the system. Figure 6 represents this trend.

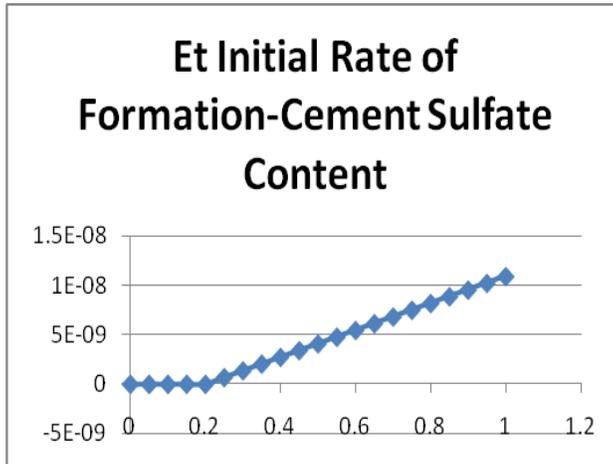


Figure 6: Ettringite formation initial rate versus cement aluminate content (for a 0.2 mole/litre cement aluminate content, and  $n = m = 1$ )

Combining the preceding equations, we have:-

$$mA_c > x_{Min} \tag{44}$$

$$nS_c - mA_c > 2x_{Min} \tag{45}$$

$$x_{Min} = \frac{f\Phi}{0.267} \tag{46}$$

$$mA_c > 3.745f\Phi \tag{47}$$

$$nS_c - mA_c > 7.491f\Phi \tag{48}$$

The DEF expansion susceptibility test will consist of two equations (47) and (48) which need to be satisfied simultaneously for expansion to occur. These conditions may equally be written as in equations (49) and (50); which in agreement with the necessary conditions for DEF occurrence, suggest that the cement sulphate to aluminate ratio should be beyond a minimal value (equation 50), and the aluminate content should be greater than a certain threshold (equation 49).

$$A_c > \frac{3.745 f\Phi}{m} \quad (49)$$

$$\frac{S_c}{A_c} > \frac{7.491 f\Phi}{nA_c} + \frac{m}{n} \quad (50)$$

Commented [S7]: check correction

## CONCLUSION

A set of two equations have been propose as a potential model for predicting the susceptibility of Portland cements to DEF-related expansive damage, basing on the chemical composition and fineness of the cement used. The first equation literally says that for expansion to occur, the cement used should contain enough alumina beyond a threshold value. The second suggests that sulphate to aluminatate ratio should be high enough for DEF-induced expansion to take place.

Both of these conditions have been reported in the literature by different authors [---]. The next step that will be dealt with in the second part of this work, is validation of the model by use of expansion experimental data from the literature.

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## REFERENCES

1. Ekolu S.O., (2004) 'Role of Heat-Curing in Concrete Durability. Effects of Lithium Salts and Chlorides Ingress on Delayed Ettringite Formation', Research and Development Bulletin, PCA RD 2869, 2004, 315 pages
2. Lawrence C.D., 'Physico-Chemical and Mechanical Properties of Portland Cements', in the 'Lea's Chemistry of Cement and Concrete', edited by Hewlett P.C., 4<sup>th</sup> Edition
3. Basista M., and Weglewski W., 'Micromechanical Modelling of Sulphate Corrosion in Concrete: Influence of Ettringite Forming Reaction', Theoretical and Applied Mechanics 35 (2008) pp 29-52

4. Weglewski W, Basista M., 'Chemically Assisted Damage of Concrete: A Model of Expansion Under External Sulfate Attack', *International Journal of Damage Mechanics* 18 (2009) 155-175
5. Tixier R., 'Microstructural Development and Sulfate Attack Modeling in Blended Cement-based Materials', PhD Dissertation, Arizona State University, Tempe, AZ., December 2000, 273 pages
6. Tixier R., and Mobasher B., "Modeling of damage in cement- based materials subjected to external sulfate attack. I: Formulation." *Journal of Materials in Civil Engineering* 15 (2003) 305-322
7. Mobasher B., and Ferraris C., 'Simulation of Expansion in Cement Based Materials Subjected to External Sulphate Attack', *Rilem International Symposium: Advances in Concrete through Science and Engineering*, March 2004
8. Heinz D., and Ludwig U., (1986), 'Mechanism of Subsequent Ettringite Formation in Mortars and Concretes After Heat Treatment', 8<sup>th</sup> International Congress on the Chemistry of Cement, Rio de Janeiro, 5 (1986) 189-194
9. Heinz D., and Ludwig U., 'Mechanism of Secondary Ettringite Formation in Mortars and Concretes Subjected to Heat Treatment', in *Concrete Durability: Katharine and Bryant Mather International Conference*, Volume 2, SP 100, American Concrete Institute, Detroit, (1997), pp 2059-2071
10. Lawrence C.D., 'Delayed Ettringite Formation: An Issue?', in *Materials Science of Concrete*, Volume IV, edited by Skalny J. and Mindness S., pp 113-154, American Concrete Society, Westerville, Ohio.
11. Taylor H.W.F., 'Delayed Ettringite Formation', in *Advances in Cement and Concrete*, edited by Grutzeck M.W., and Sarkar S.L., pp 122-131, American Society of Civil Engineers, New York
12. Kelham S., 'The Effect of Cement Composition and Fineness on Expansion Associated with Delayed Ettringite Formation', *Cement and Concrete Research* 18 (1996) 171-179
13. Lewis MC, Scrivener K.S., and Kelham S., 'Heat Curing and Delayed Ettringite Formation', In: 'Microstructure of Cement-Based Systems/ Bonding and Interfaces in Cementitious Materials, Materials Research Society Symposium Proceedings Volume 370, Massacusetts, (1994)
14. Grattan-Bellew P.E., Beaudoin J.J., Vallee V.G., 'Delayed Ettringite Formation: Effect of Clinker Particle Size and Composition on Expansion of Mortar Bars', in: Cohen M, Mindness S., Skalny J. (Editors), *Materials Science of Concrete*, Special Volume – The Sidney Diamond Symposium, American Ceramic Society, Honolulu, Hawaii, (1999) 295-307
15. Zhang Z., Olek J., Simond S., 'Studies on delayed ettringite formation in early-age, heat-cured mortars II. Characteristics of cement that may be susceptible to DEF', *Cement and Concrete Research* 32 (2002) 1737-1742
16. Shimada Y., Johansen V.C., Miller F.M., and Mason T.O., 'Chemical Path of Ettringite Formation in Heat-Cured Mortar and Its Relationship to Expansion: A Literature Review', RD136, Portland Cement Association, Skokie, Illinois, USA, 2005, 50 pages
17. Taylor H.F.W., Famy C., and Scrivener K.L., 'Delayed ettringite formation', *Cement and Concrete Research* 31 (2001) 683-693
18. Lawrence C.D., Dalziel J.A., Hobbs D.W., 'Sulfate Attack Arising from Delayed Ettringite Formation', BCA, Interim Technical Note, 12, 43 pp, May (1990)

19. Odler I., Chen Y., 'Effect of Cement Composition on the Expansion of Heat-Cured Cement Pastes', *Cement and Concrete Research* 25 (1995) 853-862
20. Odler I., and Colan-Subauste J., 'Investigations on Cement Expansion Associated with Ettringite Formation', *Cement and Concrete Research* 29 (1999) 731-735
21. Ping X., and Beaudoin J.J., 'Mechanism of Sulphate Expansion I. Thermodynamic Principle of Crystallization Pressure', *Cement and Concrete Research* 22 (1992) 631-640
22. Mehta P.K., 'Mechanism of Expansion Associated with Ettringite Formation', *Cement and Concrete Research* 3 (1973) 1-6
23. Walas S.M., 'Reaction Kinetics', *Perry's Chemical Engineers' Handbook*, Downloaded from Digital Engineering Library @ McGraw-Hill ([www.digitalengineeringlibrary.com](http://www.digitalengineeringlibrary.com)), 2004, The McGraw-Hill Companies
24. Lewis E.S., 'Investigating of Rates and Mechanisms of Reactions. Part 1: General Considerations and Reactions at Conventional Rates', 3<sup>rd</sup> Edition, *Techniques of Chemistry*, Volume VI, Wiley-Interscience, 1974, pp 129-209
25. Bensted J., and Barnes P., 'Structure and Performance of Cements', Taylor and Francis Publishing Company, 2002