

# Mathematical Modeling of the Pessimism Action of Chlorides on the Extent of Delayed Ettringite Formation. Part 1: Formulation

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## Abstract

Internal sulfate ions are the main cause of delayed ettringite formation, which leads to expansive damage of cement concretes. On the other hand, the exposure of cementitious systems to chloride ions causes corrosion of reinforcement bars that finally seriously shortens the service life of reinforced concrete structures. It has been found that, when concomitantly present in cementitious systems, chlorides interact with sulfate ions. Particularly, for a given concentration of sulfate ions present, low to moderate concentrations of chloride ions bring about serious deterioration of concretes due to high amount of ettringite formed, while higher contents of chlorides tend to reduce and even completely eliminate ettringite formation. The objective of the present project is to mathematically formulate the interaction between chloride and sulfate ions in cementitious materials. Such knowledge is useful for accurate consideration of the action of chlorides on concretes used in sea environments, thus predicting more precisely their service life (this being a far important step in design).

Kinetic analysis with pure reactants involved in individual steps implicated in the whole mechanism that pertain to the formation of, or destruction of ettringite in saline solution can be made. Monitoring each of these chemical reactions may help in establishing reaction rate equations, from which rate constants may be obtained. In the whole mechanism, it is then possible to express reaction rates of individual compounds involved, chlorides ions and ettringite included. This finally gives a system of partial differential equations of compound concentrations as a function of time, one solution of which can be put in a form of an equation of concentration of ettringite formed as a function of concentration of chlorides.

This article is the first part of a three-part study: In this part is formulated the approach (from reaction kinetics theory) followed for establishment of the mathematical equation; in the second part will be presented and discussed lab kinetics results and their use down to the mathematical model; the third and last part deals with applicability and limitations of the developed model, assessed in terms of expansion observed on steam-cured mortars made with cements used in the South African building industry.

## Introduction

In concretes cast and cured at relatively low temperatures, the ratio of sulfate to aluminate ions being high in the early development of hydration (sulfates present in cement composition are much more soluble and ionisable than calcium aluminates), ettringite is more likely to form [1, 2]. However, with the advance of hydration increasingly more aluminates pass into solution, reversing the sulfates to aluminates ratio, thus promoting the transformation of ettringite into monosulfate, which makes the concrete vulnerable to expansive damage if exposed to sulfate in the future [2-5].

When cured at high temperatures [1, 6-15] (e. g. steam-cured) around 70 to 90°C (or through the release of high heat from cement hydration by, for instance, use of hot cement and/or high cement content in massive concrete elements with concrete temperatures sometimes going over 70°C), which correspond to the temperature field of instability for ettringite, monosulfate is formed and some sulfate ions are then trapped within the body of the hydrated and solidified cement paste, with a proportion adsorbed by calcium silicate hydrates. These unused sulfate ions entrapped in such mortar and concrete microstructure constitute a potential threat for late ettringite formation (internal sulfate attack) whenever the ions are freed and usually in the presence of moisture [16, 17].

It has been found that chloride ions concomitantly present have the potential to influence ettringite crystallisation [18-20]. This influence has been suggested to be either additive or subtractive [21] depending on the concentration of chloride ions in the medium.

According to the proposed mechanism [22] of the action of chlorides on ettringite formation or destruction, under moist conditions freed sulphate ions and penetrating chlorides are competing for monosulfates. When monosulfate-containing mortars are put in water, desorbed sulfates react with monosulfates to make ettringite in somewhat small amounts. However, in the presence of low to intermediate concentrations of chlorides, the latter (chlorides) that compete with sulfates to react with monosulfates form relatively small amounts of Friedel's salts and at the same time liberates corresponding amounts of sulfate ions. These sulfates then react with the still intact monosulfates adding to the ettringite already formed, which results in large amounts of ettringite. At large concentrations, chlorides destroy both monosulfates and ettringite with the formation of large amounts of Friedel's salts and gypsum.

Basing on lab experiments conducted on pure reactants, this study aims at deriving a mathematical equation relating the concentration of chloride ions present in an environment and the extent of delayed ettringite formed. This work also involves verifying use and limitations of the equation for concretes and mortars made with local cements taking into account their chemical compositions.

### Chemical Kinetics Approach

Reaction mechanism of pure reactants involved in individual steps implicated in the whole mechanism pertaining to the formation or destruction of ettringite in saline solution are believed to be similar to those depicted in equations (1), (2) and (3) [2, 23-25]. During the formation of delayed ettringite, one molecule of tricalcium aluminate monosulfate is understood to react with two molecules of calcium sulfates, making one molecule of ettringite (a tricalcium aluminate trisulfate), as in reaction (1).

In the presence of chlorides, however, monosulfates react with chlorides in the molar ratio of one monosulfates mole to 2 moles of chlorides, leading to the formation of one mole of Friedel's salt and one mole of sulfate per mole of monosulfates, as shown in reaction (2).

In another reaction, ettringite is believed to interact with chloride ions, leading to the formation of Friedel's salt and sulfates. Yet, in this reaction, chloride ions do not just seem to replace stoichiometrically sulfate ions in the trisulfate aluminate compound as they do in their monosulfate counterpart, where two chloride ions substitute for one sulfate ion [26]. In this reaction (3) on the other hand, instead of substituting all three available sulfates, only one sulfate is believed to be substituted by chloride ions, the other two being taken off the molecule as calcium sulfates. Thus, ettringite is literally destroyed first into calcium sulfate and aluminate monosulfate and the latter then reacts with chlorides producing a dichloride substituted Friedel's salt and a further calcium sulfate molecule (chlorides affect the solubility stability of ettringite and at the same time stabilizes Friedel's salts which compete with ettringite for available alumina [27]. Reaction (3) is believed to

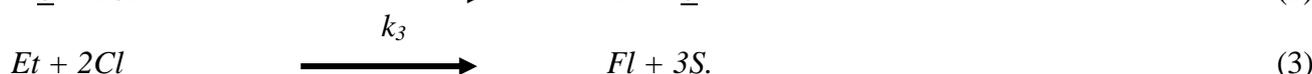
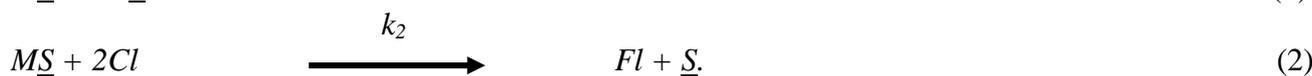
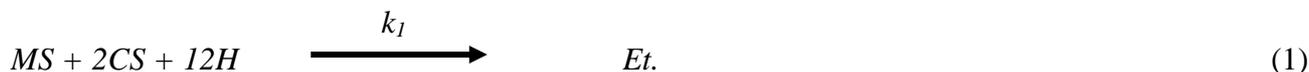
occur significantly only for high concentrations of chlorides. Kinetically, this reaction is to be considered slow and with a relatively low rate constant as compared to reactions (1) and (2).

Where  $MS = C_3A.CS.H_{18}$  (Calcium monosulfate aluminate,  $(CaO)_3.Al_2O_3.CaSO_4.18H_2O$ )

$Et = C_3A.3CS.H_{32}$  (Ettringite,  $(CaO)_3.Al_2O_3.3CaSO_4.32H_2O$ )

$Fl = C_3A.3CCl_2.H_x$  (Friedel's salts,  $(CaO)_3.Al_2O_3.CaCl_2.xH_2O$ ), and

$CS =$  Calcium Sulfate,  $CaSO_4$



$k_1$ ,  $k_2$ , and  $k_3$  being the rate constants of reactions (1), (2) and (3) respectively.

Monitoring each of these chemical reactions through kinetic analysis can help establishing the reaction rate equations (4), (5), (6), (7), (8), (9), (10), (11), (12), (13) and (14), the reaction rate of a reactant (destruction rate of a reactant or the production rate of a product), as stated by the 'Law of Mass Action' [28,29], being proportional to the product of reactants concentrations each put at a power equal to its respective partial order.

$$\frac{d[MS]}{dt} = -K_1[MS]^a[CS]^b. \quad (4)$$

$$\frac{d[MS]}{dt} = -K_2[MS]^c[Cl]^d. \quad (5)$$

$$\frac{d[CS]}{dt} = K_2[MS]^c[Cl]^d. \quad (6)$$

$$\frac{d[CS]}{dt} = -2K_1[MS]^a[CS]^b. \quad (7)$$

$$\frac{d[CS]}{dt} = 3K_3[Et]^e[Cl]^f. \quad (8)$$

$$\frac{d[Cl]}{dt} = -2K_2[Et]^c[Cl]^d. \quad (9)$$

$$\frac{d[Cl]}{dt} = -2K_3[Et]^e[Cl]^f. \quad (10)$$

$$\frac{d[Et]}{dt} = K_1[MS]^a[CS]^b. \quad (11)$$

$$\frac{d[Et]}{dt} = -K_3[Et]^e[Cl]^f. \quad (12)$$

$$\frac{d[Fl]}{dt} = K_2[MS]^c[Cl]^d. \quad (13)$$

$$\frac{d[Fl]}{dt} = K_3[Et]^e[Cl]^f. \quad (14)$$

Above equations express reaction rates of individual compounds involved, chloride ions and ettringite included (4) to (14).

With superscripts  $a$  and  $b$  partial orders of reaction (1) in regard to  $MS$  and  $CS$  respectively,

$c$  and  $d$  partial orders of reaction (2) in regard to  $M_S$  and  $Cl$  respectively,  
 $e$  and  $f$  partial orders of reaction (3) in regard to  $Et$  and  $Cl$  respectively.

Plotting the curve concentration as a function of time, reaction orders  $a$  and  $b$  for reaction (1),  $c$  and  $d$  for reaction (2), as well as  $e$  and  $f$  for reaction (3) and rate constants ( $k_1$ ,  $k_2$  and  $k_3$ ) can be obtained [29]. As all three reactions (1), (2) and (3) are of the type:



they may be assumed to be either of the 1<sup>st</sup> order (1<sup>st</sup> order in either of the reactant A or B, and of zero order in the other reactant), or 2<sup>nd</sup> order (1<sup>st</sup> order in both reactants, or second order in any one of the reactant and of zero order in the other reactant), 3<sup>rd</sup> order (1<sup>st</sup> order reactant A and 2<sup>nd</sup> order in reactant B), or even N<sup>th</sup> order (N<sup>th</sup> order in any of reactant A or B, and zero order in the other one). In each case, an appropriate integrated rate equation relating the concentration of a reactant or relative concentration of a reactant to the other, to the time will be considered. Below are integrated rate equations related to each case:

1<sup>st</sup> order reaction:

$$(-\ln[B] + \ln[B]_o) = kt \quad (\text{for a 1}^{\text{st}} \text{ order reaction in A and zero order in B}) \quad (16)$$

$$\frac{1}{2}(-\ln[B] + \ln[B]_o) = kt \quad (\text{for a 1}^{\text{st}} \text{ order reaction in B and zero order in A}) \quad (17)$$

2<sup>nd</sup> order reaction:

$$\frac{1}{[B]_o - 2[A]_o} \left( \ln \frac{[B]}{[A]} - \ln \frac{[B]_o}{[A]_o} \right) = kt \quad (\text{for a 1}^{\text{st}} \text{ order reaction in A and 1}^{\text{st}} \text{ order in B}) \quad (18)$$

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \quad (\text{for a 2}^{\text{nd}} \text{ order reaction in A and zero order in B}) \quad (19)$$

$$\frac{1}{2} \left( \frac{1}{[B]} - \frac{1}{[B]_o} \right) = kt \quad (\text{for a 2}^{\text{nd}} \text{ order reaction in B and zero order in A}) \quad (20)$$

3<sup>rd</sup> order reaction:

$$\frac{1}{[B]_o - 2[A]_o} \left( -\frac{1}{[B]} + \frac{1}{[B]_o} + \frac{1}{[B]_o - 2[A]_o} \ln \frac{[A]}{[B]} - \frac{1}{[B]_o - 2[A]_o} \ln \frac{[A]_o}{[B]_o} \right) = kt \quad (21)$$

(corresponding to a 1<sup>st</sup> order reaction in A and second order in B).

N<sup>th</sup> order reaction ( $n \neq 1$ ):

$$\frac{1}{n-1} \left( \frac{1}{[A]^{n-1}} - \frac{1}{[A]_o^{n-1}} \right) = kt \quad (\text{for a N}^{\text{th}} \text{ order reaction in A and zero order in B}) \quad (22)$$

$$\frac{1}{2(n-1)} \left( \frac{1}{[B]^{n-1}} - \frac{1}{[B]_o^{n-1}} \right) = kt \quad (\text{for a N}^{\text{th}} \text{ order reaction in B and zero order in A}) \quad (23)$$

In the determination of coefficients  $a$  to  $f$ , plots of suitable logarithm of reactant concentrations versus time are made from kinetics data, using equations given above (16 to 23). When the plot obtained is a straight line, the corresponding integrated rate equation is the one that matches with the reaction and the related orders (partial as well as global) are to be taken as those of that reaction. The rate constant  $k$  is determined as the slope of the straight line thus plotted.

Then, taking the mechanism as whole, it is possible to obtain the following reaction rate equations (on the theory that global reaction rate of a reactant taking place in a multiple reaction equals the algebraic sum of reaction rates of the substance in different steps of the mechanism [28]).

$$\frac{d[MS]}{dt} = -K_1[MS]^a[CS]^b - K_2[MS]^c[Cl]^d. \quad (24)$$

$$\frac{d[CS]}{dt} = -2K_1[MS]^a[CS]^b + K_2[MS]^c[Cl]^d + 3K_3[Et]^e[Cl]^f. \quad (25)$$

$$\frac{d[Cl]}{dt} = -2K_2[Et]^c[Cl]^d - 2K_3[Et]^e[Cl]^f. \quad (26)$$

$$\frac{d[Et]}{dt} = K_1[MS]^a[CS]^b - K_3[Et]^e[Cl]^f. \quad (27)$$

$$\frac{d[Fl]}{dt} = K_2[MS]^c[Cl]^d + K_3[Et]^e[Cl]^f. \quad (28)$$

This is a system of partial differential equations of compound concentrations as a function of time, one solution of which can be put into the form of an equation of ettringite concentration as a function of chlorides concentration.

## Conclusion

Chloride ions, when present under moist environment in heat cured cementitious systems, compete with sulfate ions in reaction with monosulfate, leading either to the formation of ettringite or Friedel's salts and gypsum. A mathematical relation between the content of chloride ions and the quantity of ettringite formed in a heat cured cementitious material may be derived from reaction rate equations of pure components involved in the delayed formation of ettringite.

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