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# The Development of Accelerated Test Method for Internal Sulfate Attack by Delayed Ettringite Formation

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**Abstract.** Delayed Ettringite Formation (DEF) is an internal sulfate attack caused by heat-induced decomposition and/or prevention of normal ettringite formed during the initial hydration of cement at elevated temperature (above about 70°C) and its re-crystallization in the hardened matrix. This reaction is a physico-chemical phenomenon inducing an expansion of the cement paste that could lead to cracking of cementitious matrix. These cracks result in a decrease in the mechanical performances and durability parameters of the material. However, the internal sulfate attack is characterized by a very slow reaction kinetics and therefore it is difficult to study it in laboratories. This research developed an accelerated method focused on mortar specimens; it is based on electrochemical techniques in order to speed the leaching of alkalis that could be accelerated the DEF.

## Introduction

Delayed ettringite formation (DEF) is a type of internal sulfate attack (ISA) observed in cementitious materials and caused by heat-induced decomposition and/or prevention of normal ettringite formed during the initial hydration of cement at elevated temperature (above about 70°C) and its re-crystallization in the hardened matrix [1 2]. DEF is a physico-chemical phenomenon inducing an expansion of the cement paste likely to lead to cracks in concrete. These cracks result in a decrease in the mechanical performances and durability parameters of the material [1,3 4]. DEF has also been identified in other prefabricated concrete elements. More specifically, this reaction has been spotted on a staircase wall of a parking lot and the stands of stadium in the United States, on post-tensioned beams and gutters in Great Britain, and inside asbestos cement roofing in Italy. In most of these prefabricated elements, disorders were observed less than 10 years after construction. DEF has been discovered in massive, cast-in-place concrete components. These observations particularly relate to foundations of electric transmission line towers and bridges in the United States, Italy and France. Such disorders began appearing between 3 and 8 years after concrete pouring [5].

The mechanism of ISA is complex depending on various factors. These factors have been classified into four groups, which are the thermal conditions at early-age, the cement-matrix composites, physical properties of the material (porosity, microcracking and strength, etc.) and the conservation environment. Famy et al. [6], in study regard to influences of the storage conditions on the dimensional changes of heat-cured mortars has concluded that leaching of alkali into the surrounding storage solution increases the rate at which sulfate lost from the C-S-H. Diamond has postulated: "leaching of alkali hydroxide from the pore solutions within the mortar specimens is required as a trigger for the sequence of responses that result in DEF derived expansions and other symptoms of distress" [7].

Numerous papers aiming to understand the reactional phenomena have been published on the DEF for several decades with a marked acceleration in recent years. However, the DEF is characterized by a very slow reaction kinetics and therefore it is difficult to study it in laboratory. The acceleration of DEF on mortars using electrical field was investigated in this study. The performance accelerated test method was evaluated by comparing the specimens with the same mixture were immersed in the deionised water and accompanied by a scanning electron microscopy.

## Experimental Study

**Materials.** CEM I 52.5 N type Portland cement from Couvrot plant -France was used for the tests. Its chemical composition and mineralogical composition are given in Table 1 and its density and Blaine fineness were of 3090 kg/m$^3$ and 4000 cm$^2$/g, respectively. In order to accelerate and amplify the appearance of expansion, 3.1% (by weight of cement) of sodium sulfate ($Na_2SO_4$) was added to the mortars [8 9], so-called Mcs mortars.

The normalised siliceous sand from Leucate (France) was a 0-2 mm French sand with a density of 2600 kg/m$^3$. This sand meets the requirements of standard CEN EN 196-1 [10] and is classified as non-reactive with respect to alkali-silica reaction [11].

Table 1 Chemical composition, mineralogical composition and Blaine fineness of cement

| Chemical composition (wt.%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $Na_2O$ | $K_2O$ | $Na_2O_{eq}$ | LOI |
| 19.5 | 5.2 | 2.3 | 64.2 | 0.9 | 3.5 | 1.07 | 0.07 | 0.77 | 2.4 |
| Mineralogical composition (wt.%) | | | | | | | | | |
| $C_3S$ | | $C_2S$ | | | $C_3A$ | | | $C_4AF$ | |
| 66 | | 13 | | | 11 | | | 7 | |

**Sample Preparation Procedure.** The mortars were made with the sand to cement ratio and a water to cement ratio are 1:3 and of 0.5 by weight, respectively. The mortar prisms were cast in 40 x 40 x 160 mm$^3$ metallic molds, according to the standard CEN EN 196-1 [10]. In addition, central reservation polystyrene with dimensions 10 x 20 x 110 mm$^3$ has been laid on the top (Fig. 1a) to place a removable anode (Fig. 1b, 1c). Moreover, regarding referent mortars Mbs that without application of accelerated method would be equipped with studs to measure the longitudinal expansion.

After casting, the moulds were covered with a plastic plate to prevent evaporation and then were submitted to a four stages thermal cycle. Initially, they were cured in a period of 2 hours at 20 ºC. In the second stage, temperature is increased with a rate of 30 ºC/ hour until reach 80 ºC. The temperature was retained at 80 ºC for 10 hours and finally decreased to reach 20 ºC for 11 hours.

Subsequently, these specimens were demoulded and tested in two methods. For one, a conventional method is implemented following Recommendations for preventing disorders due to DEF [5]. The mortars following this approach are called Mcs. Another is accelerated test method developed by the research. The mortars accompany with this method are called Mcs.A.

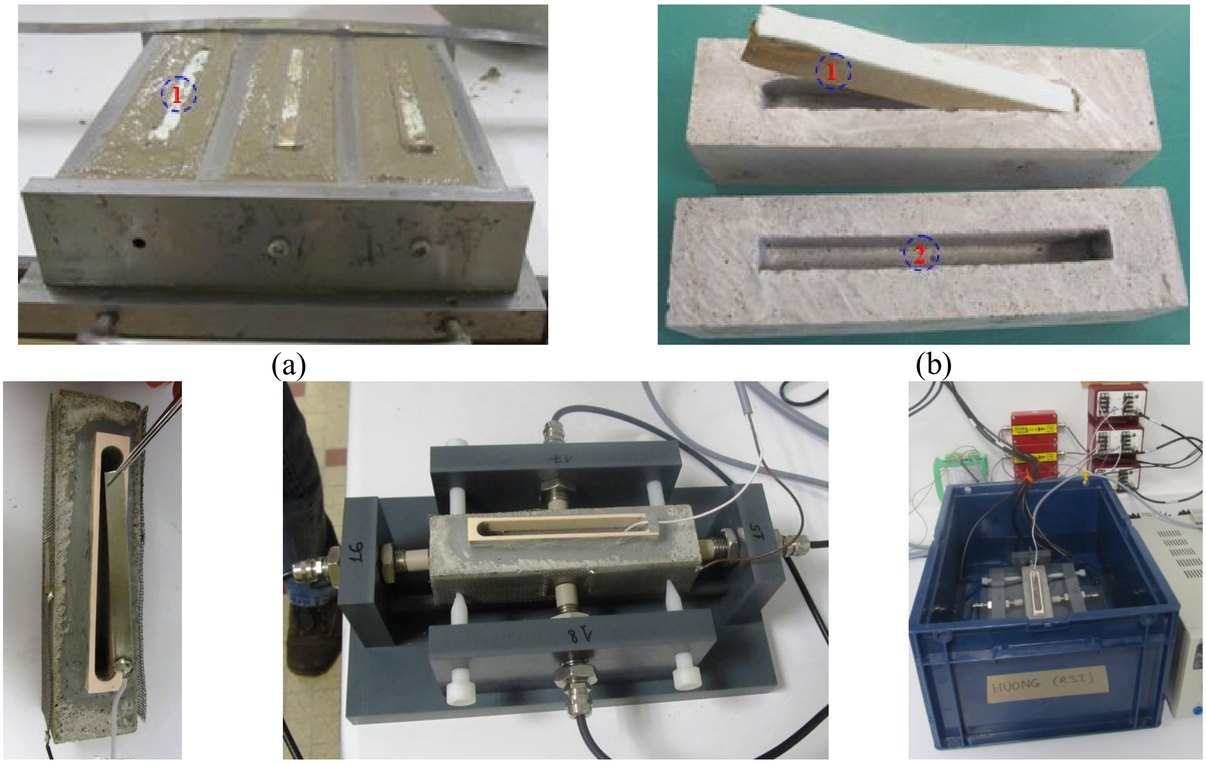
**Principle and Experimental Set-up of Accelerated Test Method.** The accelerated test method was inspired by the postulate of Diamond [7], that above mentioned. Thus, in order to accelerate alkali leaching, the specimens were exposed to an electric direct-current and using electrochemical migration that simulated the long-term alkali leaching behavior of the mortar following the same, or similar, mechanisms as natural scenarios.

Fig. 1d., 1e. show the experimental apparatus of accelerated test method. This apparatus consists of a rigid PVC cell to receive the mortar specimen and 4 eddy-current linear displacement sensors that measure expansions in both directions. The mortar was positioned in the cell by placing on two round plastic rods and four plastic screws so that the mortar can swell freely.

Since the heat produced under high-voltage direct current (such as 60V) that has a negative effect on the microstructure of cement-based materials [12], so the electrical pulse with a 10 V maximum voltage was applied in this investigation. In this study, an electrode current density of 5 A/m$^2$ (anode surface area of 20 cm$^2$) the electrical pulse cycle was applied continuously during the first 7 days, then once a week for 6 hours for 6 weeks.

**Test Procedures.** The longitudinal deformation measurement of Mcs mortars was performed in the air using an extensometer with a resolution of ±1 μm; The polished samples prepared from the

Mbs.A mortars when its expansion has reached a plateau were examined by scanning electron microscopy (SEM). The SEM used for observations is a ZEISS ЄVO®40. The polished samples were coated with a gold deposit for observations using the SEM in High-Vacuum (HV) mode.




(a) (b)

(c) (d) (e)

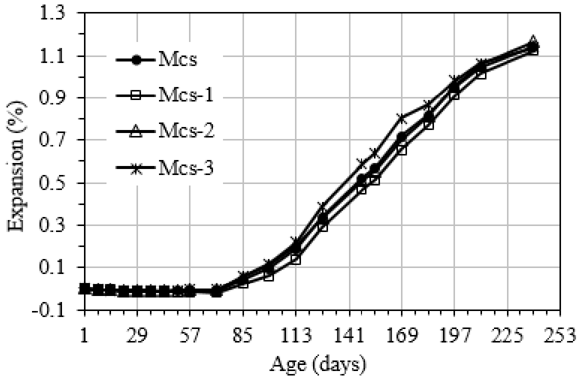
Fig. 1 Experimental apparatus for accelerated test method of mortar specimens
(1: central reservation polystyrene, 2: Central reservation for removable anode)

**Results and Discussions**

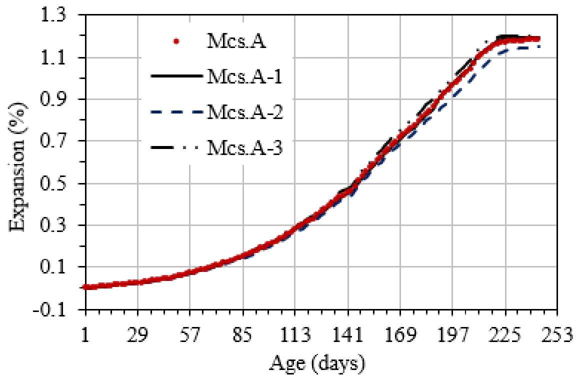
The average expansion kinetics of Mcs and Mcs. Mortar specimens that have been calculated from three different prisms for a period 245 days are plotted in Fig. 2a. and Fig. 2b., respectively. In addition, to evaluate the effectiveness of the accelerated experimental method, the Mcs and Mcs.A expansion kinetics are compared in Fig. 2c. and Fig. 2d. These curves indicate that:

- Even though the Mcs mortars have not reached ultimate expansion yet at the age of 240 days, the expansions curves develop in a sigmoid tendency generally. Which means that after an initial lag period of expansion, there would be a period of exponential expansion and ending with an expansion plateau;

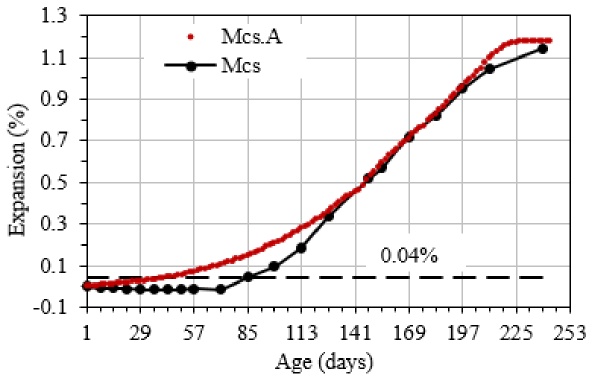
- The Mcs.A mortars have a longitudinal expansion which occurs more rapidly than those observed for control mortars (Mcs). Indeed, the onset of expansion was sooner with mortars treated by application of electric current: for Mcs, it took around 70 days to start to expand while the expansion of Mcs.A occurred as soon as the mortars have applied the method of alkaline accelerated leaching; the mortar Mcs.A showed a longitudinal expansion of 0.04% (the threshold is considered to be subjected with delayed ettringite formation) at about 35 days, while the control mortar exhibited this expansion threshold at almost 85 days; at the age about of 225 days, mortar Mcs.A had reached an ultimate expansion of 1.18%, mortar Mcs revealed expansion of 1.14% at the last measurement however, it has not reached ultimate expansion yet.



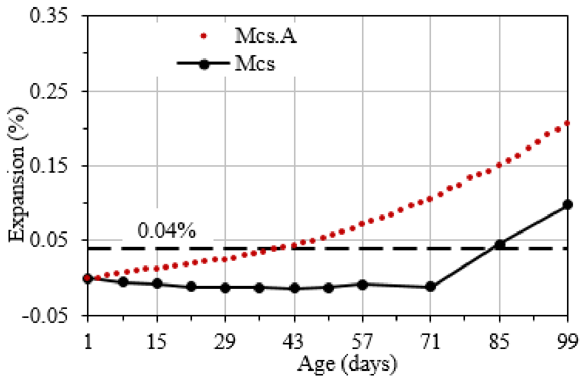

a. Longitudinal expansion of samples without application of accelerated test method.




b. Longitudinal expansion of samples with application of accelerated test method.



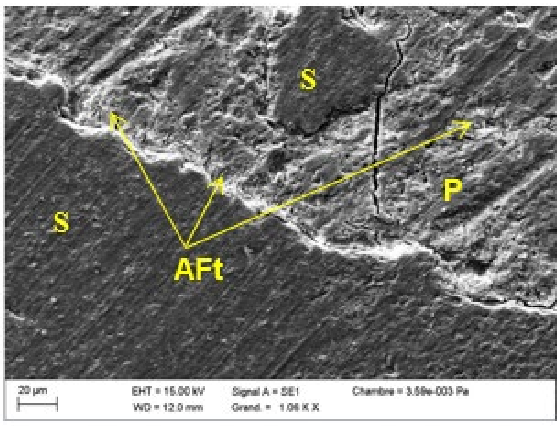

c. Longitudinal expansion of sample mortars during the test period.



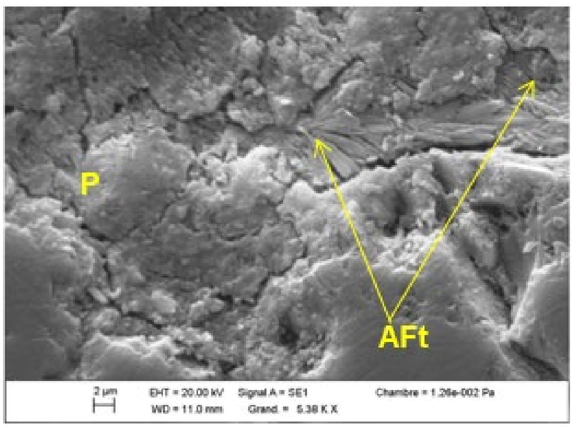

d. Zoom for expansion curves of Fig. 2c. for the first 99 days.

Fig. 2 Longitudinal expansion of sample mortars subjected to DEF with accelerated test method (Mcs.A) compared to reference samples (Mcs)

In addition, as in Fig. 3, the observations were carried out with the scanning electron microscopy of mortar subjected to an electrical pulse. The SEM images on polished surfaces of mortar Mcs.A at the end of swelling when expansion has reached a plateau (expansion of 1.18%). These SEM images illustrate that the delayed ettringite is easily observable at the paste–sand interface in the form of bands (Fig. 3a.) as well as in the cement paste (Fig. 3a. and Fig. 3b.). Moreover, we did not observe any characteristic symptoms of the alkali-reaction. This may confirm the Mcs.A expansions were due to delayed ettringite formation.




(a)




(b)

Fig. 3 SEM micrographs of mortar specimens (S: Sand, P: Paste, AFt: Ettringite)

DEF understanding has been reported that when the cement-based material temperature is higher than approximately 70°C, the primary ettringite does not form during cement hydration reactions and/or becomes decomposed. The components of ettringite must be stored, and it is suggested that excess sulfate sorbs onto C-S-H gel while aluminate either forms AFm type phases or is sorbed on the C-S-H gel, after returning to ambient temperature and in the presence of humidity, delayed ettringite is able to form or reform, this formation process leads to an expansion [1 2, 9]. The solubility of ettringite is affected by the concentration of both alkalis and $Ca^{2+}$ in the pore fluid. Besides, the presence of $K^{+}$ in the pore fluid has been shown to inhibit the formation of ettringite, allowing sulfate to enter the inner C–S–H [12]. On the other hand, according to Taylor et al. [1], the fall in the pH of the pore solution caused by leaching favours loss of sulfate from C-S-H and the consequent replacement of monosulfate by ettringite derived expansions. More recently, Nguyen et al. [8] demonstrated that an instigation of alkalis leaching into the surrounding storage solution, caused by the soaked renewal, leads to faster expansion induced by DEF. This could explain why the accelerated experimental test method is favorable to shorten experiment time if the mortar mix design has a potential risk of the internal sulfate attack induced DEF. Indeed, under an electrical DC power source which connects these two electrodes provides the potential gradient to force ionic migration. Thus, the alkaline ions ($Ca^{2+}$, $Na^{+}$, $K^{+}$) move rapidly from mortar (pore solution) into the surrounding storage solution with the application of electrical field and this leads to the acceleration of the DEF.

## Conclusions

The main conclusions of this study on development of accelerated test method for internal sulfate attack by delayed ettringite formation are drawn:

- Electrical pulse accelerated the leaching alkaline ions ($Ca^{2+}$, $Na^{+}$, $K^{+}$) from pore solution of mortar into the surrounding storage solution this leads to the acceleration of the internal sulfate attack by delayed ettringite formation. Specifically, an electrode current density of 5 A/m$^2$ (anode surface area of 20 cm$^2$) the electrical pulse cycle was applied continuously during the first 7 days, then once a week for 6 hours for 6 weeks to accelerate efficiently and without generating artifact.
- The experimental apparatus of accelerated test method that was developed by this research could be a novel method for fast evaluation of expansion behavior of internal sulfate attack due to DEF. That could facilitate for studing in laboratory and prevent mortar mixs, which risk to the pathology and likely simulate the behavior of long-term structures.

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