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# **INFLUENCE OF SULPHATE SOLUTION CONCENTRATION ON THE PERFORMANCE OF CEMENTITIOUS MATERIALS DURING EXTERNAL SULPHATE ATTACK**

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## **Abstract**

Despite the various studies on concrete submitted to an external sulphate attack in aqueous environments, this aggressive factor threatening the durability of concrete is not completely understood. A study has been made in our laboratory in order to explain the effect of the sulphate solution concentration during external sulphate attack. Length and mass measurements are registered continuously; leached calcium and hydroxide ions are also calculated. In parallel, a scanning electron microscopy observation is realized. The results show the strong influence of the sodium sulphate concentration on the kinetics of degradation: higher is the concentration, faster is the attack. It should be noted that the degradation mechanism is not really affected by the sulphate concentration which leads us to reconsider the fact that the relative proportions of expansive products depend on the sulphate concentration.

## **1. INTRODUCTION**

While sustainable development is one of our major aims, designing a durable concrete becomes a necessity. External sulphate attack, which could be defined as a reaction between sulphate ions dissolved in solution and hydration cement products causing damages, is a real threat for concrete durability in an aggressive environment. Sulphate ions are present in ground water, sea water, soils, waste waters [1], [2]. The reaction mentioned above leads to formation of gypsum, ettringite, and or thaumasite and causes cracking, spalling, softening, expansion, loss of strength and other forms of damage can occur [3].

Physical and chemical factors can influence this attack such as the pH of the solution and its concentration, the associated cation, the binder type, the water/binder ratio and the curing conditions.

Many studies were made to explain the mechanism of sulphate attacks and the influencing factors. However the complicated nature of this attack has made these studies incomplete or conflicting in several times especially that most of them do not link between physical degradation and formation of expansive products.

The aim of this study is to highlight and explain the effect of sulphate concentration on the performance of the cementitious materials in order to draw a clear schematic diagram joining

causes to effects. First we will present our experimental procedures used to evaluate this attack than we will expose our results (mass and length measurements, kinetics of leached  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions and visual and SEM observations) in order to try to explain this phenomenon.

## 2. EXPERIMENTAL PROGRAM

Mortar specimens, cast as 2x2x16 cm prisms, have been mixed with cement of type CEM I 52.5 N. Siliceous sand (Palvadeau) with a grain diameter size inferior to 2mm was chosen to avoid reactions due to calcium carbonate present in limestone aggregates [6], [7]. The water-to-cement ratio (w/c) has been chosen equal to 0.6. Mortar prisms were cured in a 100% relative humidity (RH) for 24 hours until they were demolded. Then they were stored in lime water for 14 additional days. Mortars prisms were submerged at day 15 into three different solutions of sodium sulphate ( $\text{SO}_4^{2-}$ ) with three different concentrations (3g/l; 10g/l and 30g/l of  $\text{SO}_4^{2-}$ ). In parallel, two specimens were submerged in tap water.

The prisms had gauge studs at both ends in order to measure expansion with length comparators. In addition, a resin layer was applied at these ends and also coated at 5 mm on the side. This type of protection gives us more representative and reproducible results for the length change of the entire specimen and not a part of it [6], [7]. The device used for the sulphate test is illustrated in figure 1.

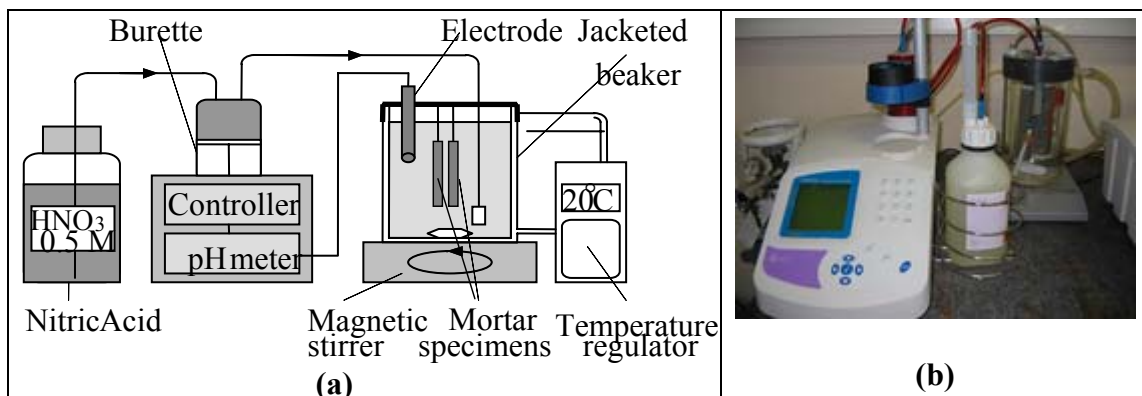


Figure 1: Schematic diagram (a) and device (b) used for sulphate test

Tests have been developed to study the effect of the concentration in controlled conditions at constant pH. The pH was regulated at 7.5 by adding a solution of nitric acid 0.5mol/l. In addition, the solutions were renewed every 15ml of added acid to maintain the concentration gradients as a constant and to avoid the interference between nitrate and cement hydrates. In fact, a neutral pH is meant to be representative of field conditions [8].

Mass and expansion were measured periodically. In parallel, a Scanning Electron Microscopy (SEM) observation and a Thermogravimetry Analysis (TGA) were made to provide us information about the products that have been formed during the attack in order to explain the obtained experimental results.

## 3. RESULTS AND DISCUSSION

### 3.1 Chemio-mechanical analysis

Mass and length of specimens have been measured periodically each time the solution is renewed (Figures 2 and 3). In parallel, the quantity of leached hydroxide ions was assessed through the added volumes of nitric acid HNO<sub>3</sub> solution, and that of leached calcium by the titration of the solutions (Figures 4 and 5).

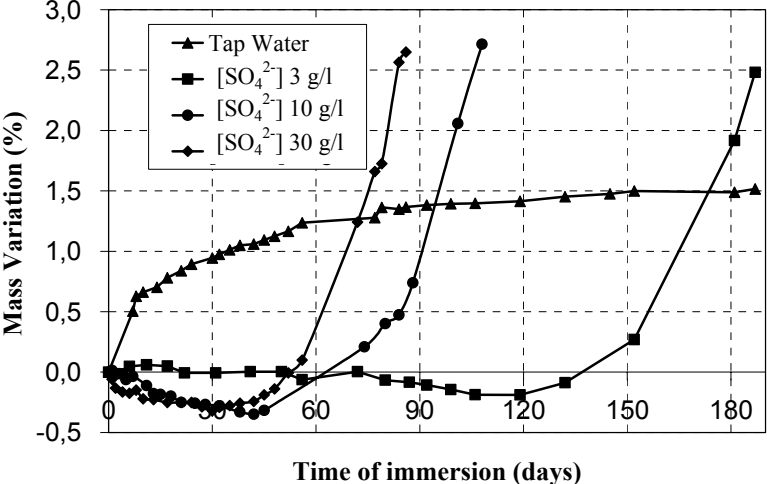


Figure 2: Mass change data for 3, 10 and 30g/l of Na<sub>2</sub>SO<sub>4</sub> solutions

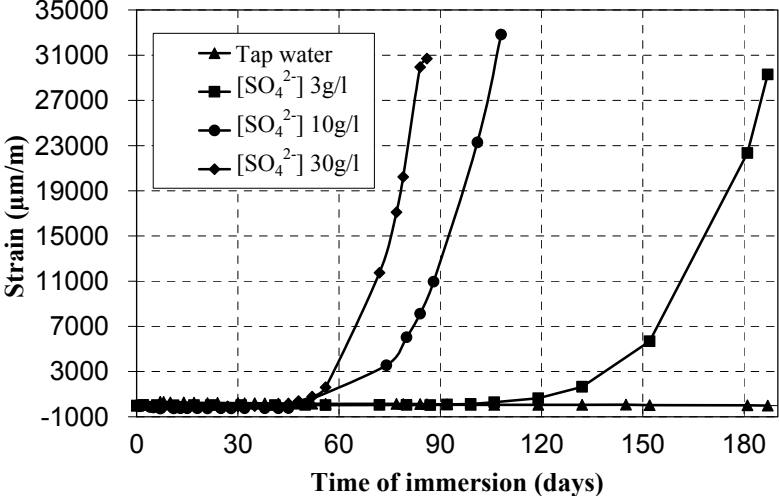


Figure 3: Expansion data for 3, 10 and 30 g/l of Na<sub>2</sub>SO<sub>4</sub> solutions

In figures 2 and 3, we can see that for any sulphate concentrations, mortar’s specimens have approximately the same response to the attack but with a delay in time with low concentrations. We can identify two stages in the evolution of the mass and the length:

- a first stage corresponding to the period of latency, when no significant expansion can be measured with a relative mass decrease caused by the leaching of portlandite,
- a second step corresponding to a mass and length increase due to swelling of damaged mortar specimens.

These results are quite similar to those obtained in other studies where these 2 phases are also distinguished on mortars immersed in sodium sulphate solutions at different concentrations varying from 2.1 g/l [9] to 30 or 34 g/l [10], [11].

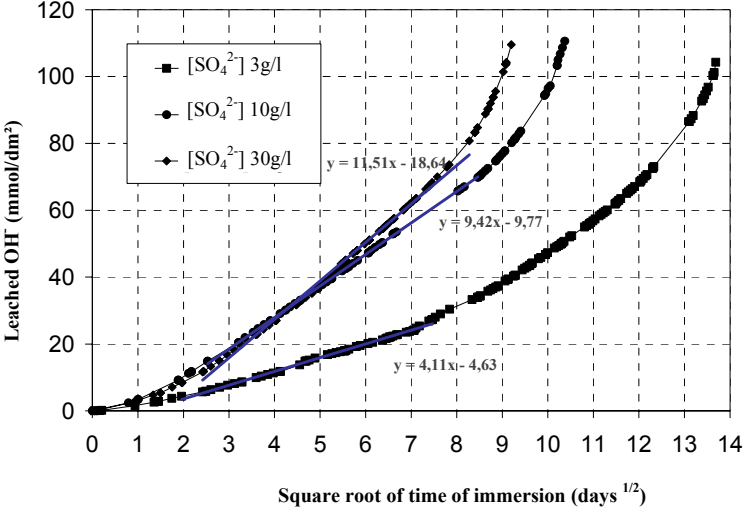


Figure 4: Kinetics of OH<sup>-</sup> leached ions in 3, 10 and 30g/l of Na<sub>2</sub>SO<sub>4</sub> solutions

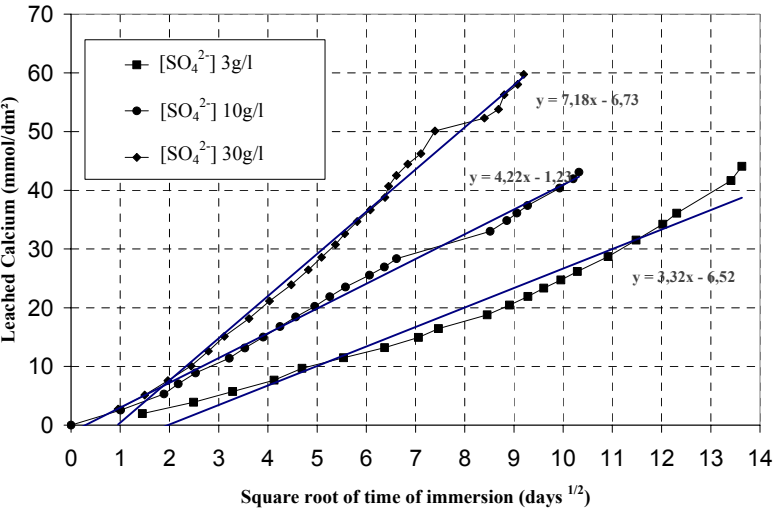


Figure 5: Kinetics of Ca<sup>2+</sup> leached ions in 3, 10 and 30g/l of Na<sub>2</sub>SO<sub>4</sub> solutions

Figures 4 and 5 show that leaching of calcium hydroxide can increase ingress of sulphate ions in cement matrix.

If we correlate these results to the mass and length variations, we can say that at the first stage, leaching is the dominant phenomenon which explains this relative decrease in mass. While in the second stage, the formation of expansive products will dominate inducing expansion and mass augmentation. We have also observed these phenomena with the nucleation of macro-cracks and by using the SEM method.

### 3.2 Visual observation

All the specimens at different concentrations were suffering from the same symptoms (figure 6).

The first visual signals of sulphate attack were longitudinal cracks on the borders of the samples. These cracks appeared at the same time when the increase of mass and length was detected. When these cracks are more developed, transversal cracks are detected and lead to a two pieces broken specimen.

E. Rozière [12] and D. Planel [9] explained in their theses these surface cracks. The formation of expansive products induce tensile strength on the central part of the specimen relatively unattacked which explains these longitudinal cracks followed by the transversal cracks leading to the disintegration of the specimen.

This length variation is accompanied with a bending phenomenon represented clearly in figure 6-d. The upper face of the specimen is affected by bleeding that's why the sulfate ions may penetrate more easily from this face than the others so a more rapid expansion can occur. One of the solutions is to reduce the w/c ratio to 0.55 or 0.5.

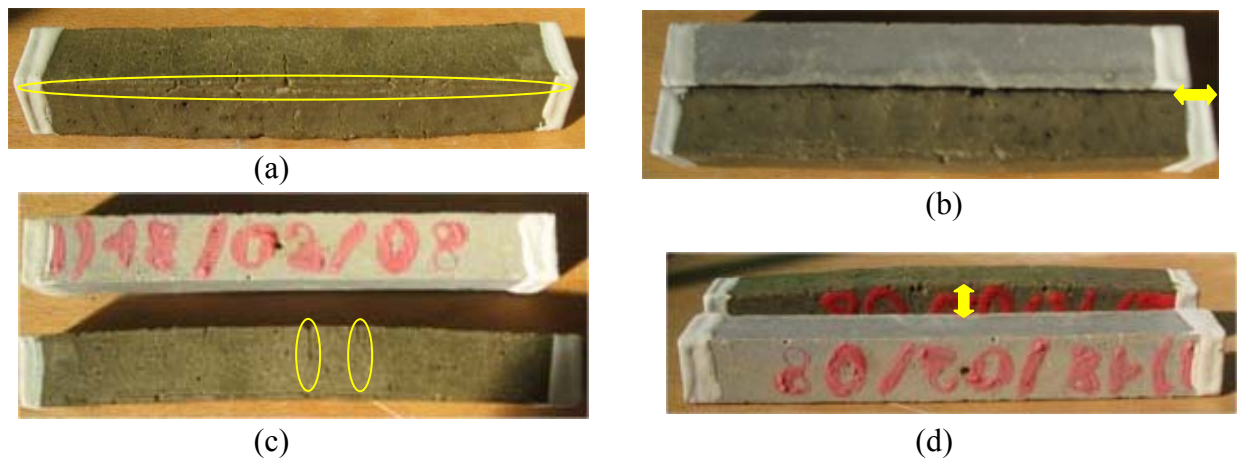


Figure 6: a) Longitudinal cracks: first visual symptoms of sulphate attack. b) Expansion of the attacked specimen compared to control specimen. c) Transversal cracks leading to the fracture of the specimen. d) Buckling phenomenon of the attacked specimen compared to control specimen.

### 3.3 SEM observation

After several observations on a SEM for different specimens exposed at three different levels of sodium sulphate concentrations at two different times, at the beginning and at the end of expansion, we can illustrate the microstructure evolution of mortars exposed to sulphate attack in figure 7.

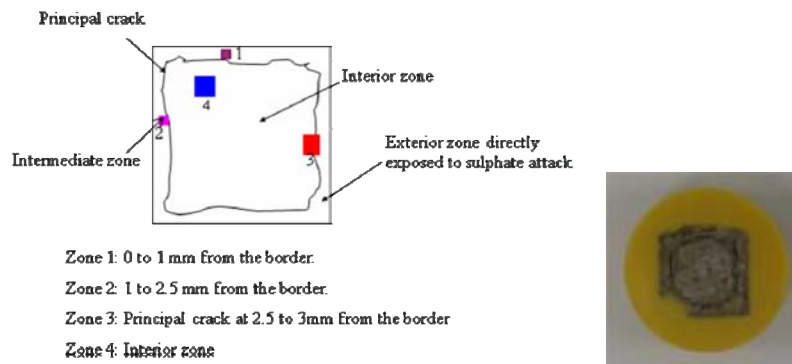


Figure 7: Schematic illustration (left) of the attacked specimen (right).

At the intermediate stage, gypsum is present in zones 1 and 2. A large crack is dividing the sample in 2 parts (figure 8): one totally disintegrated and another much more resistant.

At the end of expansion, zone 1 is totally leached and there is no more gypsum in this region. Also, C-S-H is decalcified leading to a non cohesive paste. In fact, the Thermogravimetry Analysis confirms these observations. The peak of portlandite is almost absent in region 1. In contrary, in region 4, the quantity of portlandite is most equal to that observed in the control specimen. One can observe that large voids are present in the interfacial transition zone (ITZ) around aggregate and the principal crack is much more developed. Gypsum is still present in zone 2.

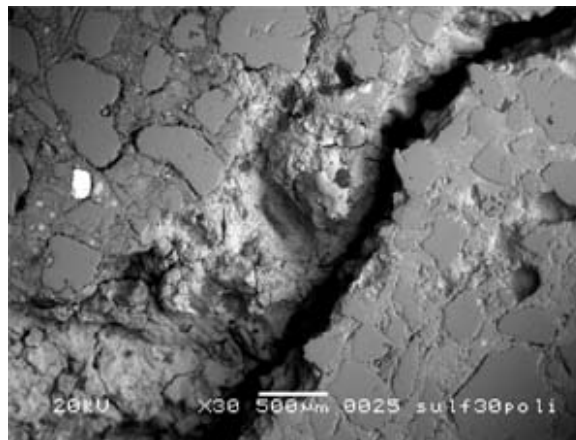


Figure 8: Large crack dividing the specimen in two parts

In fact, gypsum crystals would develop in the ITZ pores which lead to cracking and spalling and cohesion decrease. Gypsum could be found in different forms: plates, clusters, etc., as shown in figures 9 and 10. Mehta [13] explained the presence of gypsum in the ITZ: microcracks existed from the beginning in this zone. These microcracks, larger than capillary pores, are a preferential path for the creation of interconnections leading to a more permeable system. So the diffusion of sulphate ions is preponderant in this zone.



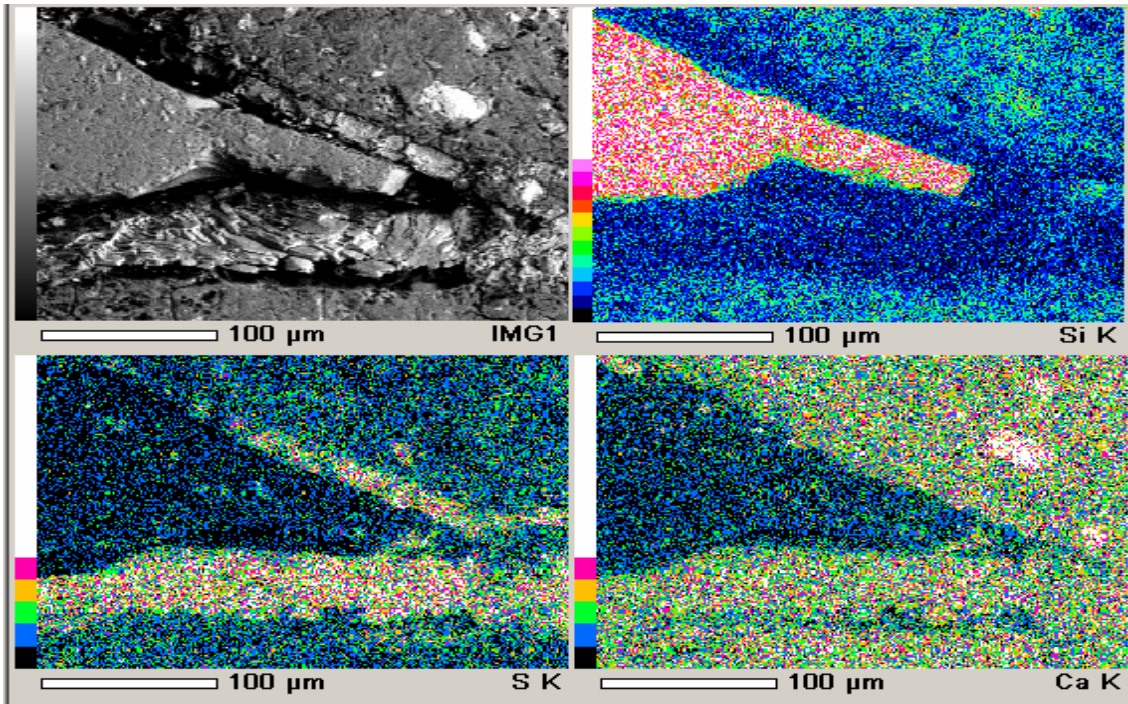


Figure 9: Energy dispersive spectroscopy analysis on an attacked mortar sample.

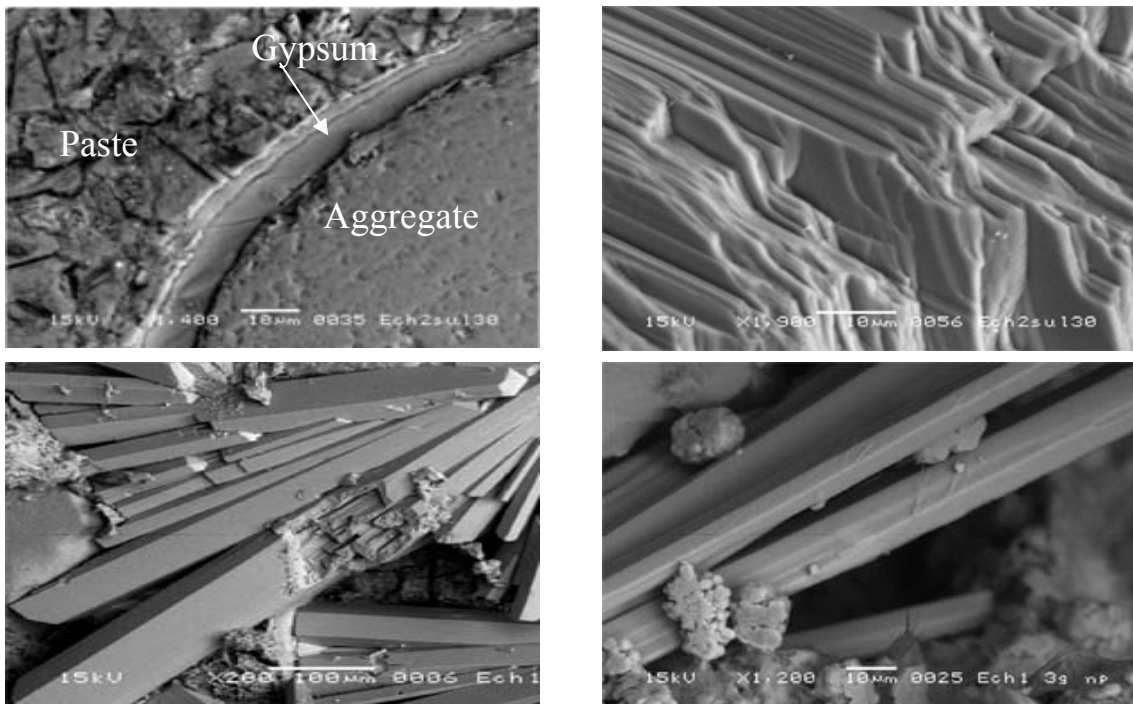


Figure 10: Different forms of gypsum crystals observed on each of the three specimens immersed in 3, 10 and 30 g/l of  $\text{Na}_2\text{SO}_4$  solution



A chemical analysis of the attacked sample has detected the presence of ettringite in small quantities especially when we get close to the specimen center.

Ettringite is not very stable at low pH (below 11.5~12) [14]. That's why it couldn't be found at the external leached zone. In fact, a study made by Mehta [15] shows that at low pH, the principal mechanism of degradation is due to gypsum formation and the quantity of  $C_3A$  (11.3% in our case) is not an influencing factor. At a constant 7.5 pH, ettringite may be transformed to gypsum and its presence is not quite certain.

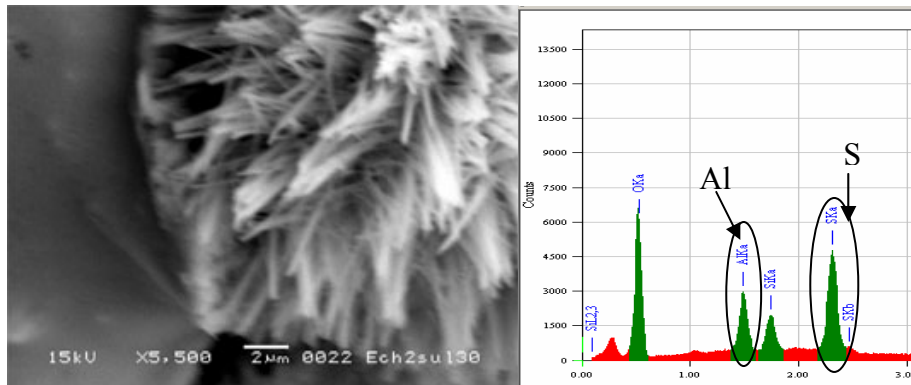


Figure 11: Ettringite spherulite existing in zone 2 cross section

#### 4. CONCLUSION

Experiments made on mortar specimens at three different sodium sulphate concentrations (3, 10 and 30g/l of  $SO_4^{2-}$ ) have shown that gypsum formation is the main cause of degradation. Also, based on the study of Mehta [15], we have shown that gypsum formation has an expansive and destructive character and it is not only the formation of ettringite that leads to expansion even with a cement rich in  $C_3A$ .

We should note that many factors are involved in the sulphate attack phenomenon. To study the effect of the sulphate concentration, other factors had been taken as a constant which may affect the obtained results. Our study is still limited to these conditions and can not be taken for a general conclusion for sulphate attack.

This study will be completed by other tests that will take into consideration the effect of the curing conditions (hydration degree and saturation rate) in order to explain and understand this complicated attack.

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