

# EFFECTS OF ALKALI-SILICA REACTION ON THE RATE DELAYED ETTRINGITE FORMATION IN STEAM CURED MORTARS

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## Abstract

From the point of view of the literature, it seems obvious that the issue of the simultaneous alkali-silica reaction and the delayed formation of ettringite in concrete, or that which occurs shortly after the first reaction, are experimentally undocumented and not fully explained. Model studies were carried out on mortar that was prepared from cement with an increased sulphate content (4% SO<sub>3</sub>) and varying alkalis content (from 0.77 to 1.63% Na<sub>2</sub>O<sub>e</sub>). Two types of aggregates were used, where one consisted of standard quartz sand and the other was of the same sand, in which 6% of the aggregate weight was replaced with opal. The results of the studies comprise steam cured mortar at 90°C. The alkalis-silica reaction was the main reason for the destruction seen in mortar with a reactive aggregate and the delayed formation of ettringite, which could have additionally contributed to the observed expansion increase.

**Keywords:** ASR, DEF, Expansion, Microstructure

## 1 INTRODUCTION

In recent years concern has developed in several countries with respect to distress observed in steam cured concrete structures, exposed to wet environments. Studies on the effect of heat curing on concrete behaviour attributed the deterioration to delayed ettringite formation (DEF) [1]. The primary ettringite that normally forms early in the hydration of Portland cement is destabilized at high temperature (above 70°C) steam curing, causing the sulphate ions from ettringite decomposition to remain in the liquid phase of hardened concrete, and precipitate as ettringite at a large age. Some sulphate ions are retained in the solid phase in the form of monosulfate and some are incorporated in the C-S-H phase. This delayed formation of ettringite was alleged to be an expansive process and the cause of the deterioration. Tepponen and Eriksson [2] reported damage to steam cured railway ties, and attributed the deterioration of to subsequent delayed ettringite formation. Possible combined effects of both ASR and DEF on Australian concrete ties were considered by Shayan and Quick [3], and Oberholster et al. [4] in studies on ties in South Africa. However, Shayan and Quick [3] reported that a sample of a deteriorated concrete sleeper exhibited considerable alkali-aggregate reaction and argued that AAR may have been a major contributor to the damage to the ties. The issue of determining the primary cause of damage to concrete elements in the presence of a combination of delayed ettringite formation and alkali-silica reaction is very controversial. This paper reports the results of experimental work on specimens in which it was attempted to enhance the formation of ASR product and ettringite either alone or in combination. Model studies were carried out on mortar that was prepared from cement with an increased sulphate content (4% SO<sub>3</sub>) and varying alkalis content (from 0.77 to 1.63% Na<sub>2</sub>O<sub>e</sub>). Two types of aggregates were used, where one consisted of standard quartz sand and the other was of the same sand, in which 6% of the aggregate weight was replaced with opal. The effect of steam curing (to 90°C) on alkali silica reaction and delayed ettringite formation (DEF) in mortar were investigated.

## 2 EXPERIMENTAL

Industrial Portland cement was used in the present study. The chemical composition and mineral composition of cement, as calculated by the Bogue method, along with its properties are shown in Table 1. In mortar marked A to D, the sulphate content in the cement was increased by the admixture of gypsum, and the alkalis content by the admixture of sodium hydroxide. Mortar marking the SO<sub>3</sub> and Na<sub>2</sub>O<sub>e</sub> content in the cement are specified in Table 2. The mortar marked A was made from standard quartz sand, and in the other mortar, standard quartz sand was used with the addition of 6% opal with a particle-size distribution from 0.5 to 1.0 mm. Mortar was made in accordance with the American ASTM C 227 standard. Mortar bars after heat treatment acc. to the diagram shown in Figure 1 were removed from the moulds. Their length was then measured (assuming the same result

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as the initial size) and they were then placed in water at 20°C. Further length measurements were made every 30 days. After 360 days of curing, the microstructure was examined using a scanning microscopy. SEM examinations were made on the specimen's fractures and micro-sections. Backscattered electrons (BSEM) were used for micro-sections surface observations as well as in selected places an x-ray analysis in a micro-area (EDX) was performed.

### 3 RESULTS AND DISCUSSION

Figure 2 shows the linear changes of the mortar versus the curing time. The heat treated mortar specimens show different degrees of expansion versus time. The expansion after 180 days for each mortar exceeded the 0.1% limit expansion. Mortar A, without an opal addition, showed the lowest expansion. Moreover, the course of its expansion was different than the course of the expansion of mortar with an opal addition. Initially, the degree of expansion was low, but after 150 days the expansion amounted to 0.1%, after which there was a quick increase. After 180 days, the elongation reached 0.2% and its further increase was again lower. This mortar did not contain a reactive aggregate. Therefore, another process could have been the reason for the expansion observed. The mortar microstructure as shown in Figure 3 is representative for mortar A. Conglomerates of fibrous ettringite exist in this mortar, which is created from entangled fibre spherical forms that exist in voids (Figure 3a) as well as the ettringite layers on the surface of aggregate grains (Figure 3b). The ettringite layers' location on the surface of the sand grains is characteristic for delayed ettringite formation [5]. The obtained results were different than those presented by Shayana and Ivanusec [6], who showed that in mortar without a reactive aggregate, despite the application of cement with a composition that is favourable to increase the ettringite content, no expansion occurred. However, in the experiment carried out, only delayed ettringite formation could have been responsible for the expansion occurrence.

The specimen of mortar B, which contained a reactive aggregate showed an especially high degree of expansion in the first months of curing and its expansion after 150 days was three times higher than the expansion of mortar A. In addition, curing in water causes lower gains of the bars' elongation. The mortar B microstructure (cement of the same composition as mortar A, aggregate with opal addition) after 360 days of curing is shown in Figures 4 and 5. In this mortar, a small part of the opal grains reacted with sodium and potassium hydroxides, in turn forming potassium-sodium-calcium silicate (Figure 4), in which solid ettringite exists on the sand grains' surface, creating layers up to 30  $\mu\text{m}$  thick (Figure 5 a). In Figure 5 b, ettringite that filled the voids is also shown, and its presence has been confirmed by its microanalysis. The results of the studies carried out after 360 days show the existence of sodium-potassium-calcium silicate gel and a secondary ettringite. There are no grounds to assume that the secondary ettringite does not also originate in specimen B (proven by SEM observations, Figure 5).

Figure 6 shows a comparison of the expansion of the mortar without a reactive aggregate with the expansion of the mortar of the same composition with the reactive aggregate. Mortar B expansion after 360 days was approx. 15% higher compared to mortar A's expansion. It is most likely that the delayed ettringite formation in specimen B does not result in an expansion. This may be caused by earlier micro-cracking that was triggered by the alkalis-silica reaction, in which ettringite may crystallise, as well as by ettringite formation in the voids. This is confirmed by the low expansion of specimen B or even its absence between 150 and 360 days. The expansion of opal containing specimens, during curing up to 60 days to the largest extent, depends on the alkali content in the cement (Figure 7). Subsequently, up to 150 days, a similar increase in the specimens' lengths was observed (by ca. 0.3%) and further curing in water caused smaller gains of the bars' elongation.

In mortar with a higher sodium and potassium content in the cement (marked C and D), the total corrosion of the opal grains was observed and the formed sodium-potassium-calcium silicate gel swelling caused numerous cracks in the cement matrix (Figure 8). Ettringite layers also exist in those mortars, partly covering the sand grains' surface (Figure 9). The cracking of the mortar bars, quickly increases in the expansion during the initial curing period and also the existence of potassium-sodium-calcium silicate gel result from the alkalis reaction with opal included in the silica aggregate. This is confirmed by the existence in the mortar of a large amount of silica aggregate with alkali reaction products. The opal grains reacted entirely with sodium and potassium hydroxides, as shown in Fig. 8. In all the studied opal grains there was a large sodium and potassium content, in which the calcium content was the highest in the outside grain's zone and move down towards their core. It may be presumed that the elevated steaming temperature (90°C) of the mortar with a high content of sodium and potassium and with a reactive aggregate could have accelerated the alkalis-silica reaction. Similar results were obtained by Diamond and Ong [7], who found that the application of heat treatment

accelerated the alkalis-silica reaction and subsequent mortar storage under humid conditions, which is an additional factor. In later studies, Diamond [5, 8] also found that the expansion and damage of mortar that occurs within the initial weeks after steaming in the case of cement with a high sodium and potassium content, was caused by the alkali-silica reaction.

The composition of cement used in the tested mortar was favourable for the creation of increased ettringite content. Wieker et al. [9] showed that during heat treatment there are often conditions wherein ettringite is not stable and the delayed formation of ettringite depends on the alkalis content in the liquid phase and occurs only after a longer period of curing in the air saturated with water vapour or in water. Ettringite decomposition in cement with high alkalis content proceeds faster and the ettringite formation under conditions of mortar curing after steaming occurs with a delay. Because of the high content of sulphate and sodium and potassium oxides content in the cement, in all the studied mortars, the  $\text{SO}_3/\text{Na}_2\text{O}_e$  mole ratio in the liquid phase of the mortar, after heat treatment, could have been high. Referring to the ion concentrations in the liquid phase in equilibrium with the ettringite containing solid phase as calculated by Glasser [10], it should be expected that the conditions for ettringite formation during further curing occurred in all the mortars. Hence, in the experiment in the mortar of the cement with simultaneous high sulphates and alkalis content, there were conditions during steaming, in which the ettringite was not stable.

Furthermore, Taylor et al. [11], in discussing the results of Kelham [12] studied the alkalis addition influence, and found that the expansion is higher at higher sodium and potassium content in cement and at the same time it is rich in  $\text{SO}_3$ . According to Taylor et al. [11] there are two reasons that may explain this observation. Firstly, the increase in sodium and potassium content may cause a higher degree of alite hydration at the early stage of hardening, and the formed C-S-H phase adsorbs sulphate ions during heat treatment. Secondly, sodium and potassium hydroxides increase the solution's pH in the pores, which then creates favourable conditions for monosulphate formation. As a result, in the C-S-H phase, and in the solution in the mortar pores after heat treatment, there is a higher content of sulphate ions, which during further curing may form a delayed ettringite. Delayed ettringite formation reduces the sulphate ions content in the solution in the concrete pores, and at the same time to ensure the equilibrium, the hydroxyl ions concentration increases.

The expansion of mortar bars with reactive aggregate between the 60<sup>th</sup> and 360<sup>th</sup> day of curing (Fig. 2) may be partially caused by the alkalis-silica reaction, but it may also result from delayed ettringite formation. Delayed ettringite formation, as shown by Divet and Randriambolona [13], is favoured by a reduction in basicity that is caused by the alkalis-silica reaction or alkalis leaching from the mortar while the specimens cured in water. The results of Escadeilas [14] confirm that a high sodium and potassium content increases the risk of the occurrence of the expansion of heat treated mortar from cement with a high sulphate content. Furthermore, Brown and Bothe [15] state that ettringite formation is delayed upon the presence of a solution in the pores with a high concentration of sodium and potassium hydroxides, which occurs in the case of cement with a high content of those respective components. Instead, the alkalis-silica reaction decreases the sodium and potassium hydroxides concentration and may be favourable towards ettringite formation.

#### 4 CONCLUSIONS

The present research carried out showed that:

Delayed ettringite formation is the reason for the destruction of the steam cured mortar with a non-reactive aggregate and industrial cement (0.77%  $\text{Na}_2\text{O}_e$ ) with an increased sulphate content (4%  $\text{SO}_3$  in cement). This mortar shows the highest expansion between the 150<sup>th</sup> and 180<sup>th</sup> day of curing. Observations of its microstructure confirm the existence of ettringite layers on the sand grains' surface and in the pores.

The alkalis-silica reaction is the main reason for the destruction in steam cured mortar with the cement with a composition as stated above and with a reactive aggregate with the delayed formation of ettringite that could additionally contribute, to a small extent, to an expansion increase.

In steam cured mortar with cement with an increased alkalis content (1.49% or 1.63% of  $\text{Na}_2\text{O}_e$ ) and increased sulphate content (4%  $\text{SO}_3$ ) and reactive aggregate, the value of the initial expansion (up to 60 days) depends on the alkalis content in the cement and this expansion may result from the alkalis-silica reaction. This is confirmed by the observation of sodium-potassium-calcium silicate gel microstructure in the places of opal grains. The ettringite formed layers on the aggregate grains' surface and that fill the cracks in the cement grout may also be responsible for the expansion in the later periods. The observed similar increase in the mortar specimens' length (by approx. 0.3% up to 150 days), irrespective of the alkalis content in the cement, may prove that a process different than the alkalis-silica reaction may bring about the expansion.

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TABLE 1: Chemical composition, mineralogical composition and cement specific surface.

Chemical composition, [%]									
SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Na <sub>2</sub> O <sub>e</sub>	Loss ignition
21,02	2,86	5,79	63,14	0,90	2,89	0,21	0,85	0,77	1,89
Mineralogical composition, [%] and cement specific surface									
C <sub>3</sub> S	βC <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	C <sub>2</sub> S̄	H <sub>2</sub>	S [cm <sup>2</sup> /g]			
58,08	17,12	9,30	8,79	4,90		3340			

TABLE 2: Mortars symbol, SO<sub>3</sub> and Na<sub>2</sub>O<sub>e</sub> contents in cement.

Mortar symbol	A*	B	C	D
SO <sub>3</sub> content, [%]	4,0	4,0	4,0	4,0
Na <sub>2</sub> O <sub>e</sub> content [%]	0,77	0,77	1,49	1,63
*without of opal				

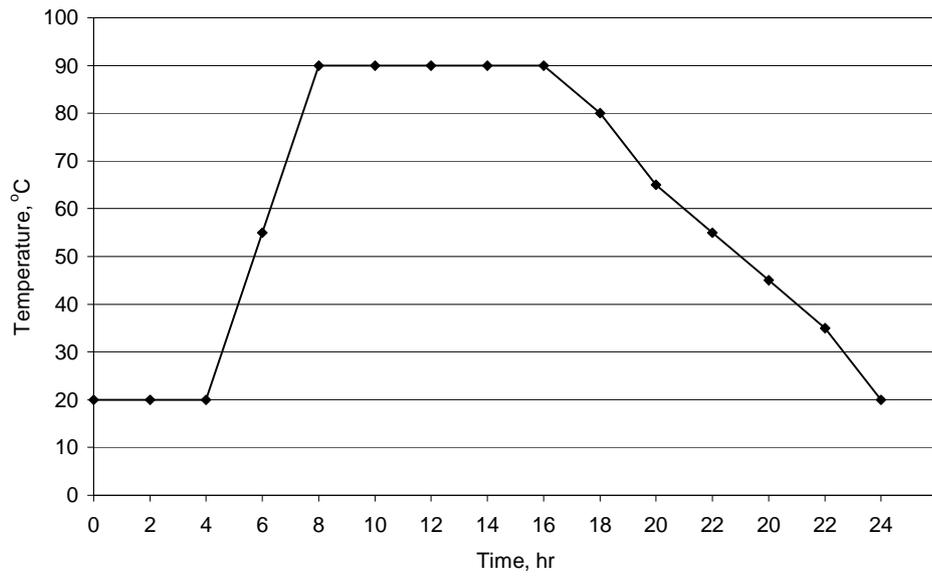


Figure 1: Steam curing at maximum temperature 90°C.

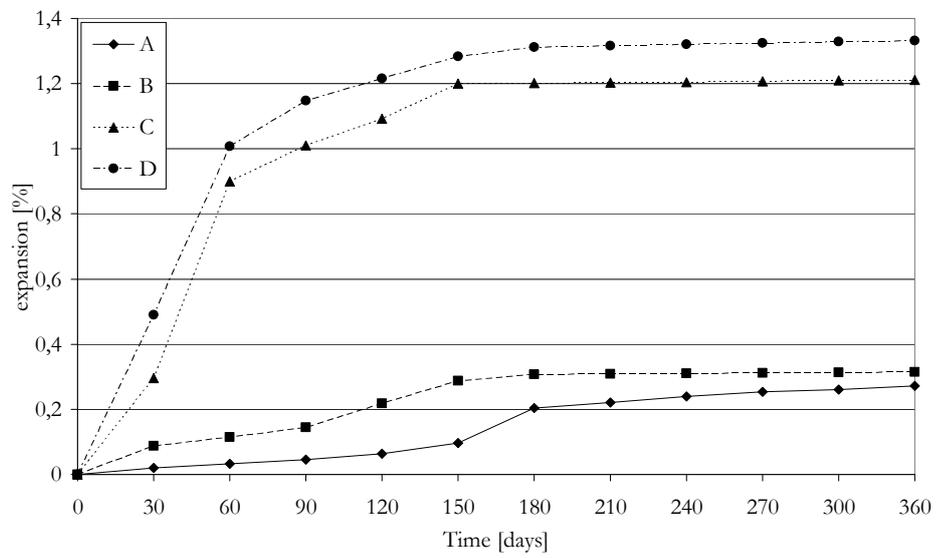


Figure 2: The linear changes of the mortar versus the curing time.

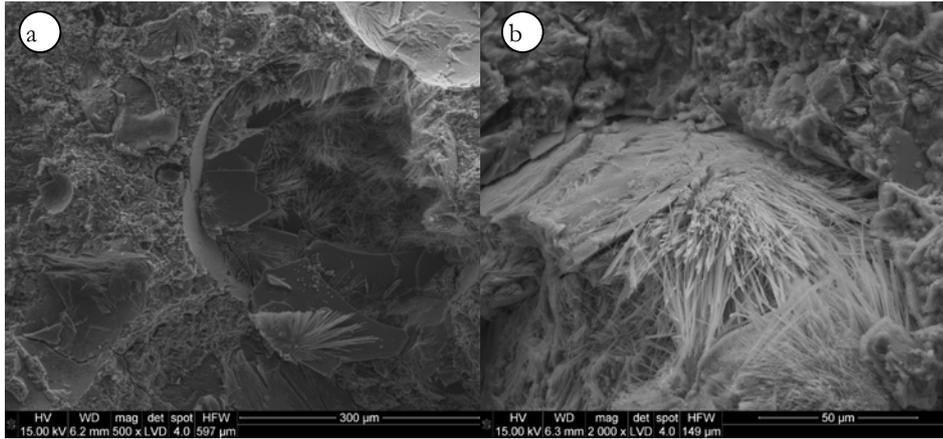


Figure 3: The microstructure of steam-cured mortar A after 360 days of curing in water, industrial cement, and quartz sand; a) conglomerates of fibrous ettringite in voids, b) ettringite layers on the sand grain surface.

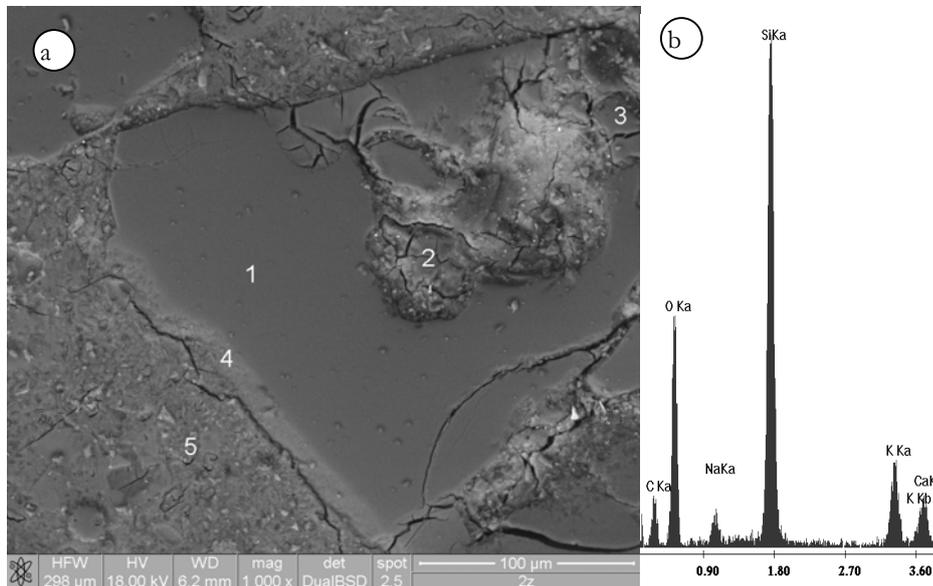


Figure 4: Sodium-potassium-calcium silicate in the place of an opal grain (mortar B), a) micro-section observations in backscattered electrons, b) x-ray analysis in micro-area 2.

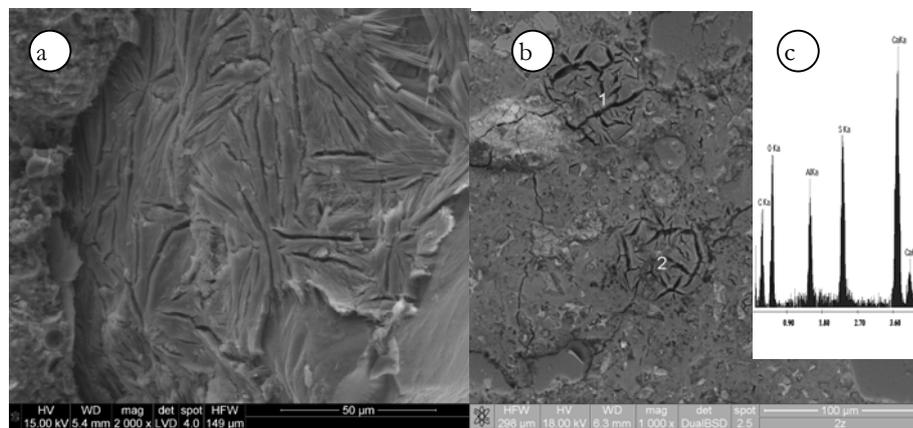


Figure 5: a) Ettringite on the surface of an aggregate grain (mortar B), b) solid ettringite in voids, micro-section observations in backscattered electrons, c) x-ray analysis in the ettringite micro-area.

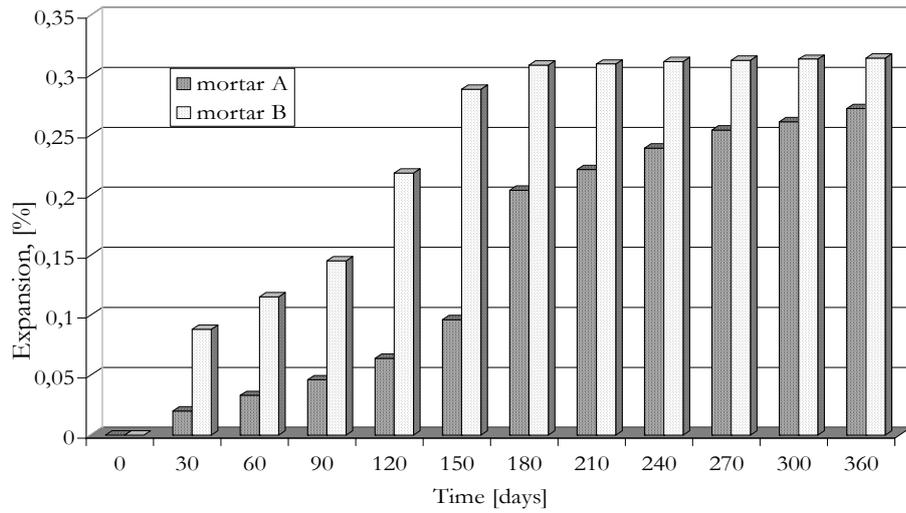


Figure 6: Comparison of mortar A expansion (without a reactive aggregate – dark columns) and mortar B expansion (with a reactive aggregate – light columns).

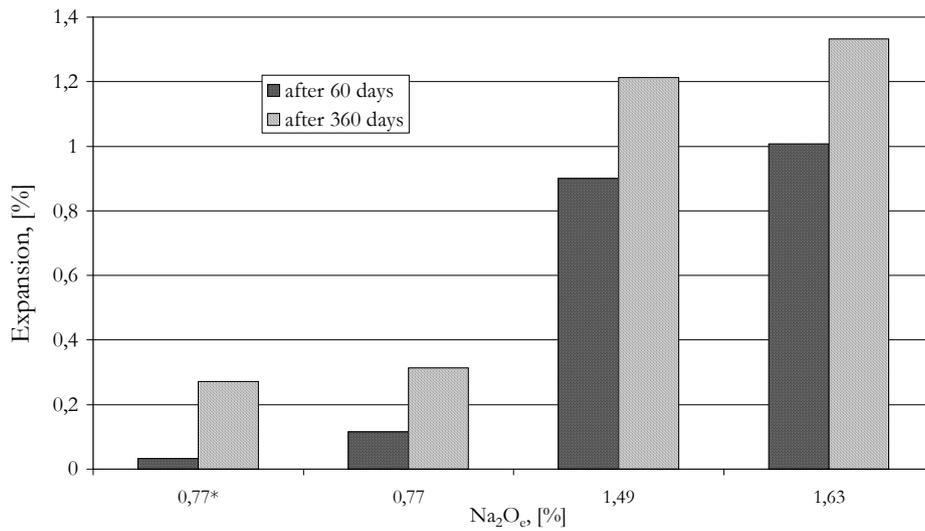


Figure 7: Influence of Na<sub>2</sub>O<sub>e</sub> content in cement on mortar expansion after 60 and 360 days.

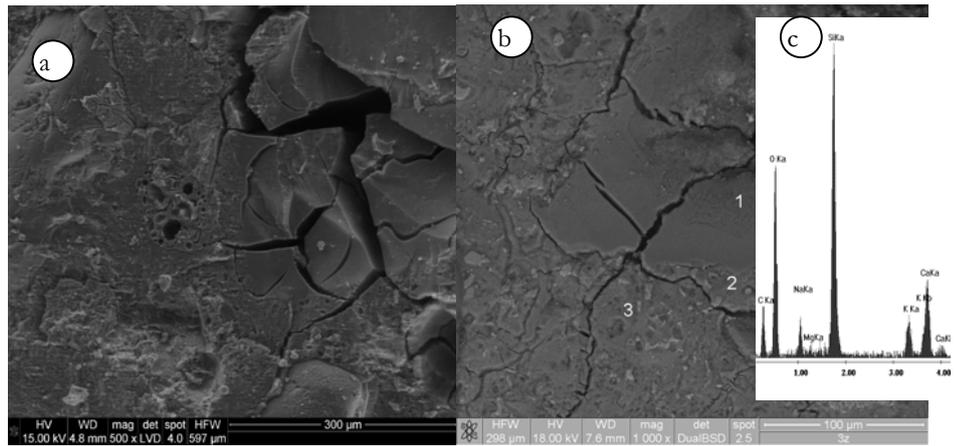


Figure 8: a) Sodium-potassium silicate in the place of an opal grain, b) potassium-sodium-calcium silicate gel, micro-section observations in backscattered electrons, c) x-ray analysis in micro-area 2(mortar C).

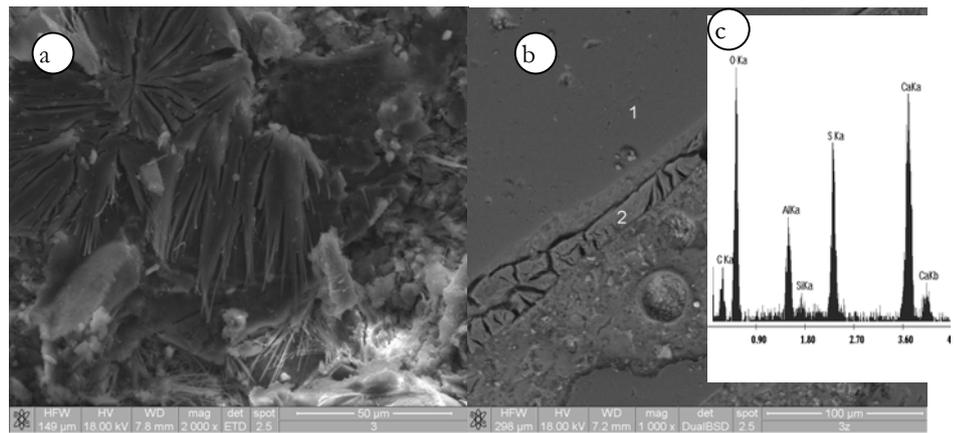


Figure 9: a) Ettringite layers on a sand grain, b) ettringite filling a crack around a sand grain, c) x-ray analysis in ettringite micro-area (mortar C).