Pergamon

Cement and Concrete Research 31 (2001) 795–803

CEMENT AND CONCRETE RESEARCH

# Influence of the storage conditions on the dimensional changes of heat-cured mortars

C. Famy[a,b,*], K.L. Scrivener[b], A. Atkinson[a], A.R. Brough[a,1]

[a] Materials Department, Imperial College, London SW7 2BP, UK
[b] Laboratoire Central de Recherche, Lafarge, 38291 Isle d'Abeau, France

Received 7 July 2000; accepted 12 February 2001

**Abstract**

Some cementitious materials cured at elevated temperature may expand on subsequent exposure to moisture. Concern has been expressed as to the relevance of small laboratory specimens to field concretes, in particular due to the potential leaching of ions into the storage solution. The work presented here aims at investigating this effect. Mortars cured at elevated temperature in identical fashion were subsequently stored at 90–100% relative humidity (RH) and in water, a LiOH solution, and KOH solutions of various concentrations. The largest and most rapid expansion occurred with mortars immersed in water. The samples stored at 90–100% RH expanded more slowly. Expansion was even slower when subsequent storage was in LiOH or KOH solutions. The same samples were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). These techniques indicated that ettringite had formed over time in all samples, with little apparent relation to the degree of expansion. The composition of the C-S-H gel changed over time, differently for the different storage conditions. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Heat treatment; Storage conditions; Ettringite; Alkali leaching; EDX

## 1. Introduction

In the last 10 years, much attention has been paid to the potential expansion of some Portland cement concretes cured at elevated temperatures. This phenomenon has been attributed to the formation of ettringite in hardened concretes [1–5] and is known as delayed ettringite formation (DEF). However, ettringite is very often detected in mature concretes showing no expansion [6]. Because the small crystals of ettringite present in the cement paste are unstable relative to larger ones (due to their greater specific surface area) they tend to recrystallise in any available spaces such as large cavities, cracks and air voids [6]. This process occurs in both damaged and undamaged concretes or mortars irrespective of the curing temperature and is innocuous [6–10]. This is one reason why no direct correlation has been established between the amount of ettringite detected and expansion of heat-cured mortars [11–15].

In order to determine the parameters involved in the expansion mechanism, extensive laboratory studies have been carried out, especially to study the influence on expansion of curing conditions and cement composition [2–5,11–20]. The curing temperature was shown to be the critical factor for expansion to occur. Many laboratory studies carried out on pastes, mortars or concretes under controlled conditions have shown that expansion does not occur if the material has not been subjected to a temperature above ~70°C, but that it may occur if the specimen has experienced temperatures higher than this [2–5,11–20]. For such mortars, no general relationship between expansion and cement composition exists [4,5,12,13,19]. It was concluded that a suitable choice of Portland cement composition cannot guarantee the avoidance of expansion in materials that have experienced temperature above 70°C.

---

[*] Corresponding author. Lafarge, 95 rue Montmurier, BP15, 38291 Saint Quentin Fallavier, France. Tel.: +33-474828125; fax: +33-474828011.

*E-mail address*: charlotte.famy@pole-technologique.lafarge.com (C. Famy).

[1] Present address: CEMU, Departments of Materials and Civil Engineering, University of Leeds, Leeds LS2 9JT, UK.

PII: S0008-8846(01)00480-X

While the effect of curing conditions and cement composition relating to expansion have been widely investigated, very little work has been carried out on the influence of storage conditions after the heat treatment. In most of the studies on DEF, the heat-cured specimens were immersed in water following heating to accelerate expansion. Heinz and Ludwig [3] showed that mortars submerged in water expanded faster and to a greater extent than those exposed to humid environments, and that those maintained under dry conditions did not show any expansion. Recently questions have been raised on the influence of leaching of alkalis, which undoubtedly occurs in specimens stored in large volumes of water [16].

In this study, various storage conditions were investigated:

- Immersion in water.
- Storage at 90–100% relative humidity (RH).
- Immersion in a LiOH solution.
- Immersion in KOH solutions of different concentrations.

These particular storage conditions were selected to understand the extent to which the storage environment after the heat treatment affects expansion. In addition to expansion measurements, the effect of the storage conditions on the microchemical and microstructural changes was also investigated.

## 2. Experimental

The mortar specimens were prepared using an ordinary Portland cement (65.5% CaO, 21.9% $SiO_2$, 5.4% $Al_2O_3$, 3.9% $SO_3$, 1.1% $K_2O$, 0.1% $Na_2O$ and 2.2% $Fe_2O_3$), which was selected for its known expansive behaviour when used in mortars heat-cured at 90°C. The siliceous aggregate was a German Normensand meeting standard DIN EN 196-1. The mortar prisms were cast in $16 \times 16 \times 160$ $mm^3$ moulds. The water/cement ratio and the sand/cement ratio were 0.5 and 3, respectively. After casting, the mortar specimens were tightly covered, placed in individual sealed plastic bags in which water containers were placed to maintain a high humidity and precured at 20°C for 4 h (Fig. 1). They were then placed in a water tank where the temperature was increased at a rate of 30–35°C/h to 90°C. The temperature was maintained at 90°C for 12 h. At the end of the heat treatment, they were allowed to cool naturally to 20°C until 1 day after mixing. The prisms were demoulded and then subsequently stored under different conditions: in water, at 90–100% RH, in KOH solutions and in a LiOH solution. As a reference, a mortar was cured at 20°C for 1 day and stored in water at 20°C.

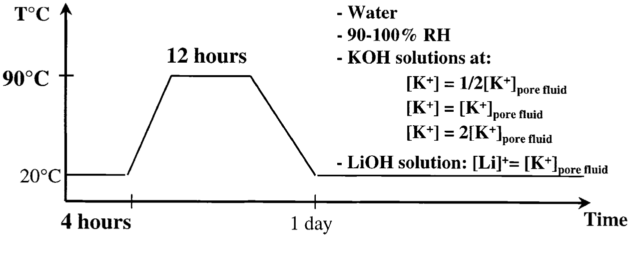

Fig. 1. Curing regime applied to mortars showing the various storage environments studied.

Table 1
Percentages of $Na^+$ and $K^+$ leached out from the pore fluid into the storage solutions for the 90°C cured mortars stored for 300 days either in water or at 90–100% RH or in the [P]KOH solution

| Storage conditions | Percentage $K^+$ leached out | Percentage $Na^+$ leached out |
|---|---|---|
| Water | 96 | 95 |
| 90–100% RH | 85 | 80 |
| $[P]_{KOH}$ | 0 | 98 |

For the storage at 90–100% RH at 20°C, the prisms were placed above the water level in a sealed container. Due to the temperature cycles in the laboratory there was some vaporisation and condensation of water on the prisms.

Three different KOH concentrations were chosen based on the potassium concentration of the pore fluid of the mortar directly after heat-curing. Using a pore-pressing device, this concentration was found to be 460 mmol/l. The storage solutions used were of this concentration, twice as concentrated (920 mmol/l) and half as concentrated (230 mmol/l). They will be referred to as [P]KOH, [2P]KOH and [1/2P]KOH, respectively. The [P]KOH thus approximated to a simulated pore solution. The LiOH solution had the same molar concentration as the [P]KOH.

The KOH storage solutions of various concentrations gave information with respect to the influence not only of the extent of alkali leaching but also its rate on the expansive behaviour of heated mortars. The $K^+$ and $Na^+$ concentrations of the storage solutions were monitored by inductively coupled plasma spectrometry and the fractions of each cation leached then estimated from the alkali contents of the cements, the cement contents and masses of the mortars and the volumes of the storage solutions. Table 1 shows the results at 300 days. Leaching was very substantial for the mortars stored in water and somewhat less so for those stored at 90–100% RH, but for those stored in the simulated pore solution containing 460 mmol/l KOH, virtually all the $Na^+$, but none of the $K^+$ was leached. For the mortars stored in water, 80% of the $K^+$ and 60% of the $Na^+$ were leached during the first 10 days (Fig. 2). The storage solutions were also analysed for $SO_4^{2-}$; only minor quantities were leached [13]. Therefore, alkalis going into storage solution were balanced by $OH^-$, thus lowering the pH in the pore solution.

Expansion measurements were recorded every week. Expansion was measured as the change in length relative

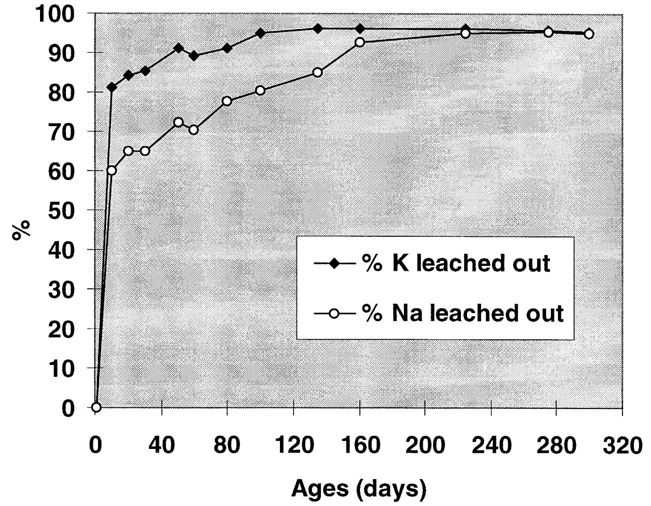

Fig. 2. Percentages of potassium and sodium leached out from the pore solution of the heat-cured mortars stored in water.

to the original length (measured at 1 day). The overall expansion was determined as the average expansion of three prisms.

The development of crystalline phases was studied by X-ray diffraction (XRD) immediately after heating and after various intervals during subsequent storage. The XRD analyses were performed on specimens without prior drying, as it was observed that any form of drying (solvent or freeze-drying) affected the crystallinity of the ettringite. A 10% rutile was added as an internal standard to all specimens after they had been very gently ground into a fine powder and passed through a 90-μm sieve to remove most of the aggregate particles. The resultant mixtures were loaded into diffractometer sample holders from the back to minimise preferred orientation. A calibration curve allowed the patterns to be corrected for the quartz aggregate (3.34 Å peak) and the amount of ettringite (9.73 Å peak) was calculated on an arbitrary scale by determining the ratio of the integrated peak areas of ettringite and rutile. When prepared in this way, the amount of ettringite measured was found to be reproducible between nominally similar samples and the relative heights of the secondary peaks indicated that the degree of preferred orientation was not too significant.

In parallel, specimens for examination by scanning electron microscopy (SEM, JEOL JSM 35-CF equipped with a solid state backscattered electron [BSE] detector and an energy dispersive X-ray analyser) were freeze-dried to stop further hydration. They were then vacuum impregnated with epoxy resin, lapped to a flat surface with 9 μm alumina and polished successively with 3, 1 and 1/4 μm with diamond paste. A carbon coating was applied to the polished sections to improve their conductivity. The microscope was operated at an accelerating voltage of 15 kV.

## 3. Results

### 3.1. Expansion measurements

Fig. 3 shows the expansions of the mortars cured at 90°C for 12 h and subsequently stored in water, at 90–100% RH and in the KOH solution having the same concentration as the pore fluid ([P]KOH). No significant expansion was recorded for the mortars cured at 20°C for times up to more than 800 days, which is in agreement with previous findings that expansion is associated with elevated curing temperatures.

All the expansion curves for the heat-cured mortars showed the same characteristic steps: an induction period before expansion starts, expansion at a fairly uniform rate and levelling off to a plateau. The fastest and greatest expansion was given by the mortars immersed in water. The expansion has already started to level off by 200 days, reaching an ultimate expansion of 1.0% between 400 and 600 days.

The mortars stored at 90–100% RH expanded more slowly. At 200 days they had barely started to expand, although at 600 days they were approaching an ultimate level of expansion of 0.85%, which is lower than that of the mortars kept under water.

The mortars immersed in the [P]KOH solution expanded much more slowly than either of the above and at 900 days showed no sign of levelling off. After a storage of 300 days in the [P]KOH solution, one of the three prisms was removed and immersed in water. This led to a dramatic increase in the rate of expansion.

The behaviour of the mortars stored in the [P]KOH solution, and particularly the change in expansion rate on moving to a water storage, indicate that the suppression of leaching by storage in a simulated pore solution reduces the rate of expansion.

Fig. 4 compares the expansions found on storage in the three KOH solutions, the LiOH solution and water. The rate of expansion increases with decreasing KOH concentration of the storage solution. No expansion was detected in the

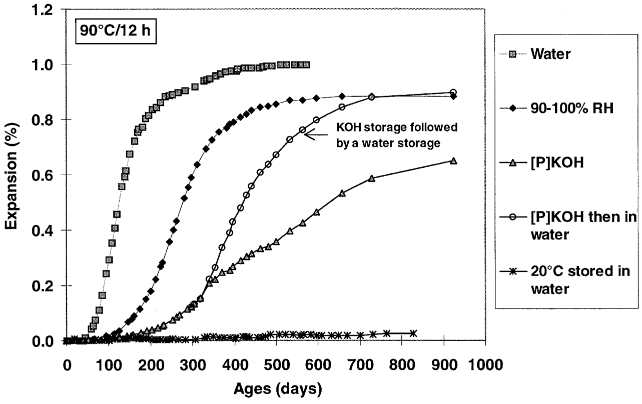

Fig. 3. Effect of postheat treatment storage conditions on expansion of mortars heated at 90°C for 12 h.

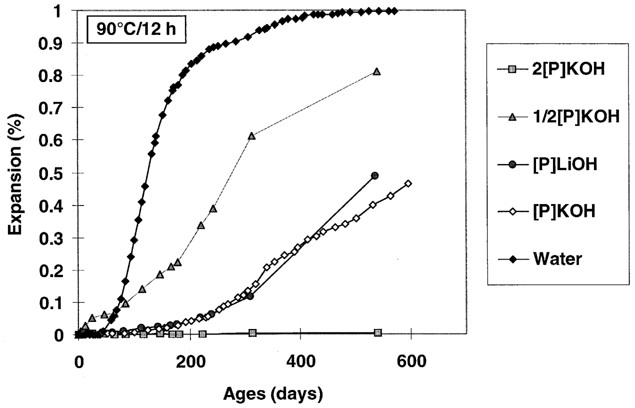

Fig. 4. Effect of storage solutions concentrations on the expansions of mortars heated at 90°C for 12 h.

mortars immersed in the most concentrated [2P]KOH solution, even after a 540-day storage. Fig. 4 also shows that substitution of the [P]KOH solution by a [P]LiOH solution does not significantly affect the expansion, which thus does not depend on the nature of the alkali ion.

### 3.2. X-ray diffraction

When the mortars are cured for 1 day at 20°C, 3.4 arbitrary units (a.u.) of ettringite have formed in the mortars (Table 2). After a 400-day storage in water at 20°C, the amount of ettringite increases to 5.6 a.u. This increase in ettringite content in ambient cured mortars is probably due to minor amounts of carbonation [16,21]. It takes place without expansion.

Table 2
Relative amounts of ettringite in the 90°C cured mortars subsequently stored in different environments

| Storage conditions | Amount of ettringite (a.u.) | Percentage expansion (90°C) |
|---|---|---|
| *20°C cured mortars* | | |
| 1 day | 3.4 | 0 |
| 400 days | 5.6 | 0 |
| *90°C cured mortars* | | |
| 1 day | No ettringite detected | 0 |
| 200 day-storage | | |
| Water | 5.8 | 0.81 |
| 90–100% RH | 5.5 | 0.17 |
| 0.5[P]$_{\text{KOH}}$ | 4.6 | 0.28 |
| [P]$_{\text{KOH}}$ | 4.0 | 0.05 |
| 2[P]$_{\text{KOH}}$ | No ettringite detected | 0 |
| [P]$_{\text{LiOH}}$ | 1.9 | 0.04 |
| 400 day-storage | | |
| 20°C cured mortars/water | 5.6 | 0 |
| Water | 5.9 | 0.97 |
| 90–100% RH | 5.8 | 0.78 |
| [P]$_{\text{KOH}}$ | 4.3 | 0.27 |
| 600 day-storage | | |
| Water | 6.0 | 1.00 |
| 90–100% RH | 5.3 | 0.87 |
| [P]$_{\text{KOH}}$ | 4.0 | 0.46 |
| 300 days in water following 300 days in KOH | 4.6 | 0.80 |

The ettringite contents measured in the 20°C cured mortars at 1 and 400 days are also presented.

In contrast to the situation at 20°C, no ettringite was detected by XRD directly after heating at 90°C, but a poorly crystalline solid solution approximating to calcium monosulphoaluminate had formed (Fig. 5). During a subsequent 200-day storage, ettringite has formed in all the mortars except those immersed in the most concentrated [2P]KOH solution (Figs. 5 and 6).

Table 2 gives the relative contents of ettringite in the different specimens at different storage times. The highest amount of ettringite is found in the water-stored mortars for all periods of storage. There is no significant difference between the ettringite contents of the mortars stored for 200 days in water (5.8 a.u.) and at 90–100% RH (5.5 a.u.) but the degrees of expansion differ markedly (0.81% and 0.17%, respectively, Table 2). A further 200-day storage slightly increases the amount of ettringite and the gap between the degrees of expansion becomes smaller.

Decrease in the KOH concentration of the storage solutions increases the relative amount of ettringite (Table 2). When the mortars are immersed in the [P]KOH solution, 4.0 a.u. of ettringite has developed in 200 days but almost no expansion has occurred (0.05%). On the other hand, for a storage period of 600 days, expansion has reached 0.46% and the ettringite content remains the same.

The mortars initially immersed for 300 days in the [P]KOH solution and then stored in water for 300 days contain more ettringite (4.6 a.u.) than those kept for 600 days in the KOH solution (4.0 a.u.) (Table 2). This amount is still lower than that found in the mortar stored for 600 days in water (6.0 a.u.).

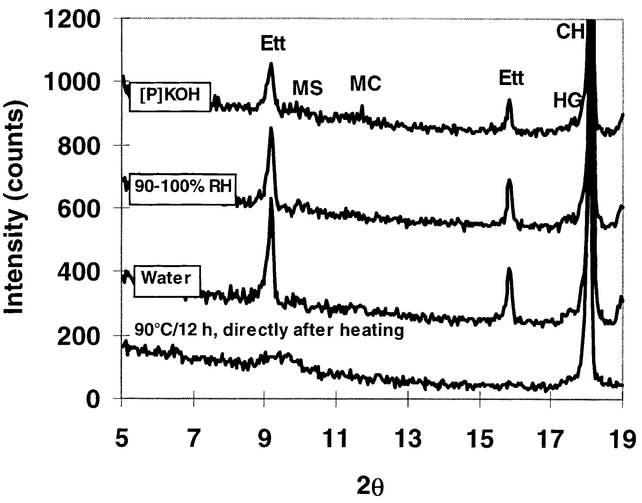

Fig. 5. XRD patterns of the 90°C/12 h cured mortars directly after heating and after storage for 200 days in water, at 90–100% RH or in [P]KOH solution. Ett = ettringite, MS = calcium monosulphoaluminate, MC = calcium monocarboaluminate, and HG = hydrogarnet.

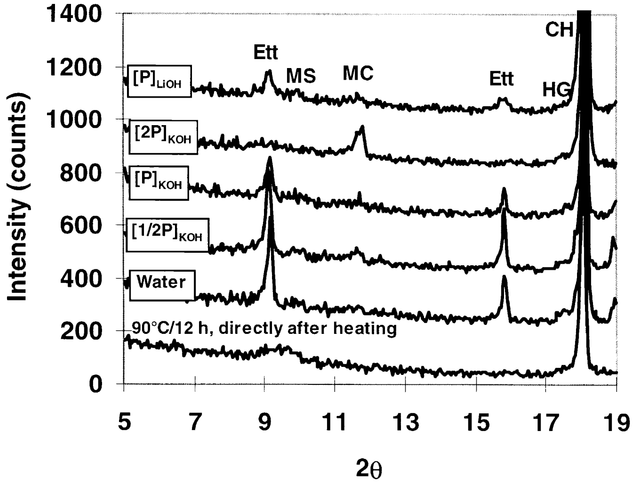

Fig. 6. XRD patterns of the 90°C/12 h cured mortars directly after heating and after storage for 200 days in KOH solutions of various concentration. Abbreviation as in Fig. 5.

These results show that:

- No direct correlation exists between the amount of ettringite formed after heating and the degree of expansion.
- The amount of ettringite developed over time depends on the storage conditions after the heat treatment and especially on the rate of leaching of alkali hydroxide from the pore fluid to the surrounding storage solution. A high KOH concentration in the storage solution delays the formation of ettringite because the slowness of leaching maintains a high ettringite solubility.

### 3.3. Scanning electron microscopy

The microstructure of the control mortars cured at 20°C for 1 day displays the typical features widely described previously [22,23], such as the presence of very thin hydration rims (less than 1 μm) around but separated from the cement grains, and a large amount of porosity (Fig. 7). In agreement with the XRD results, ettringite deposits are detected dispersed throughout the microstructure. They exhibit a microcracked aspect due to partial dehydration during specimen preparation and in the high vacuum chamber of the SEM.

Directly after the heat treatment at 90°C, thick rims of inner C-S-H have developed around the cement grains (Fig. 8). Some hollow shells are observed where the cement grains have totally reacted leaving space delimited by C-S-H. No ettringite crystals are detected, which is consistent with the XRD results. Crystals of calcium monosulphoaluminate are found. Clusters of $Ca(OH)_2$ are observed within the paste and around aggregates.

After 200 days, the mortars stored in water have already expanded by 0.8%. The microstructure reveals the presence of two-tone inner C-S-H formed around cement grains (Fig. 9). The outer lighter C-S-H rims have formed during heat-curing at 90°C. During subsequent storage in water at 20°C, anhydrous grains have further hydrated forming the darker innermost C-S-H [13,24]. Some cement grains have been totally hydrated, leaving a darker inner C-S-H core surrounded by a lighter C-S-H rim. Ettringite deposits are found in air voids and cavities.

Gaps filled or partially filled with ettringite are present at the paste/aggregate interfaces. This microstructural feature has been previously observed in mortars which have expanded following heat-curing [1,6,12–17,20] and in mortars damaged by freeze–thaw [20,25]. Such gaps have been proposed to result from the difference in thermal expansion coefficients of the cement paste compared to that of quartz [26]. However, the fact that gaps are not

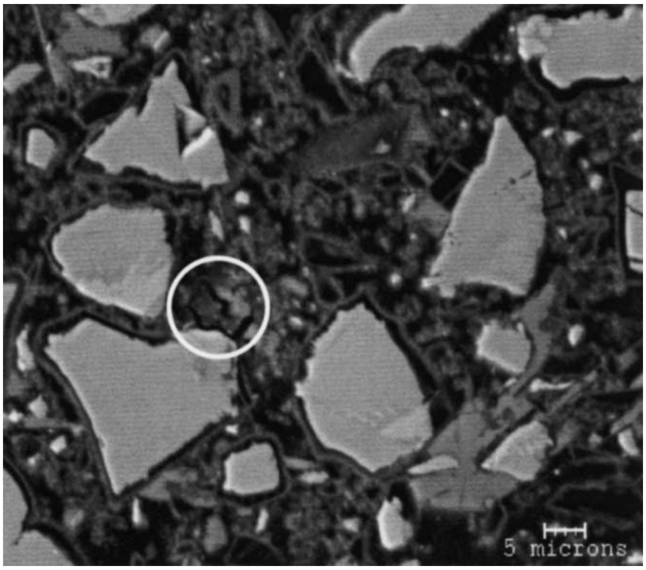

Fig. 7. BSE image of the microstructure of a 20°C cured mortar after 1 day of hydration. Ettringite has formed within the structure (circle).

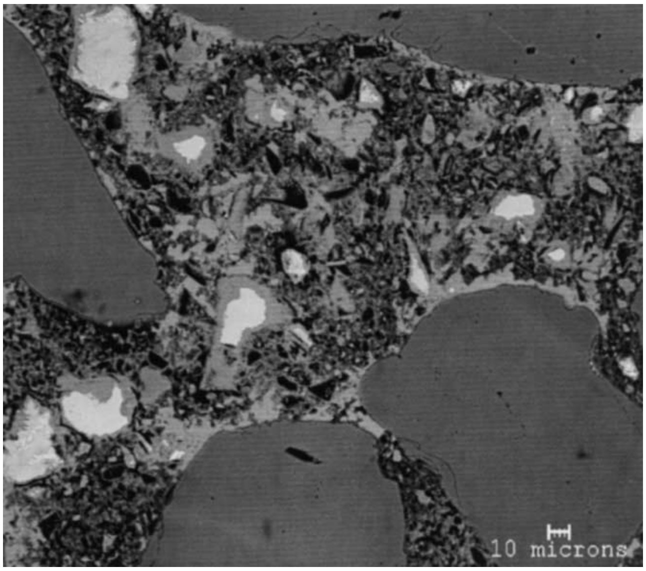

Fig. 8. BSE image of the microstructure of a 90°C/12 h cured mortar after 1 day of hydration; no subsequent storage.

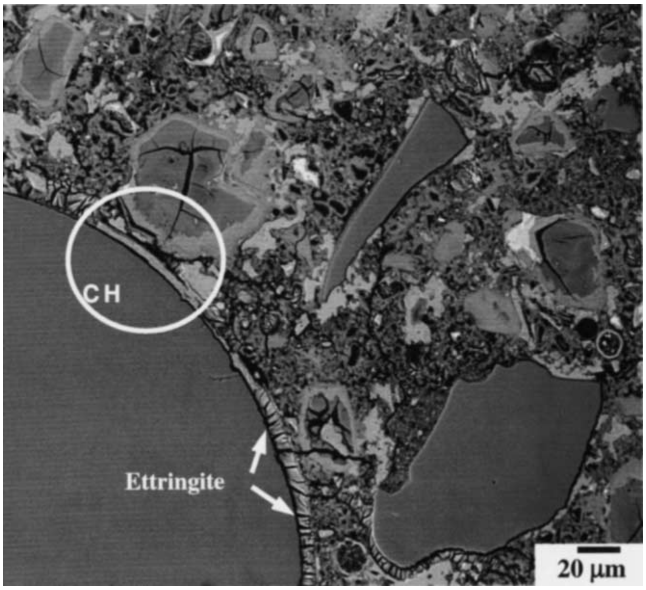

Fig. 9. BSE image of a 90°C/12 h cured mortar stored in water for 200 days. Ettringite and CH deposits have filled in the gaps formed at the paste/aggregate interfaces. Two-tone C-S-H has developed around clinker grains.

observed in heat-cured mortars which do not exhibit any expansion suggests that they are associated with the expansion process.

Some of the features observed in the mortars stored for 200 days at 90–100% RH humidity or in the [P]KOH solution are similar to those detected in the water stored specimens, such as the presence of two-tone C-S-H rims and ettringite deposits in air voids and cavities (Figs. 9–11). However, a significant difference is noted. In the mortars stored at 90–100% RH, which have expanded by only 0.17%, narrower gaps around aggregates have formed, and they are generally empty (not filled with ettringite) (Fig. 10).

Gaps are not detected in the specimens immersed in the [P]KOH solution which has not expanded significantly (0.04%) at this stage (Fig. 11).

It appears that gap width is related to the degree of expansion. When mortars have expanded significantly (as in the water stored mortars, 0.8% expansion), wide gaps are observed. On the other hand, in specimens experiencing lower degrees of expansion (as in the 90–100% RH stored mortars, 0.17% expansion), smaller gaps have formed. These microstructural observations support the view that gaps are *not* caused by the formation of ettringite at the paste/aggregate interfaces as previously proposed in the literature [4,5,14,27–29] but are likely to come from an expansion of the paste [12,13,16,20,30,31] as when gaps are firstly formed, there is no ettringite detected in them.

The other storage conditions, such as in the [1/2P]KOH and [2P]KOH solutions and the [P]LiOH solution, do not lead to any significant differences in the microstructural development of the mortars and are therefore not discussed.

### *3.4. EDS microanalyses of the inner C-S-H product*

The EDS microanalyses were made on the inner C-S-H product and especially on the lighter inner C-S-H rims formed during heat treatment. Microanalyses of the darker inner C-S-H product (developed over storage at 20°C) are reported elsewhere [13]. For statistical accuracy about 25 point microanalyses were acquired for each specimen, each from a rim around a different cement grain. The micro-

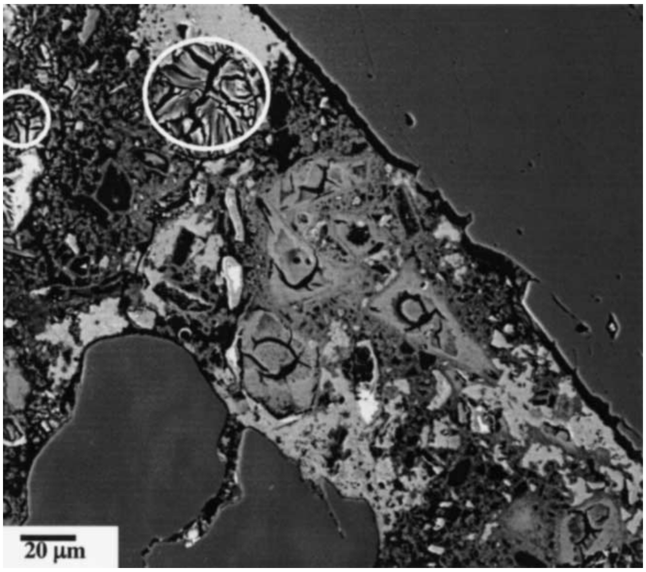

Fig. 10. BSE image of a 90°C/12 h cured mortar stored at 90–100% RH for 200 days. Ettringite deposits in air voids and cavities are observed (circles). The gaps at the paste/aggregate interfaces can be observed but most of them are free of ettringite.

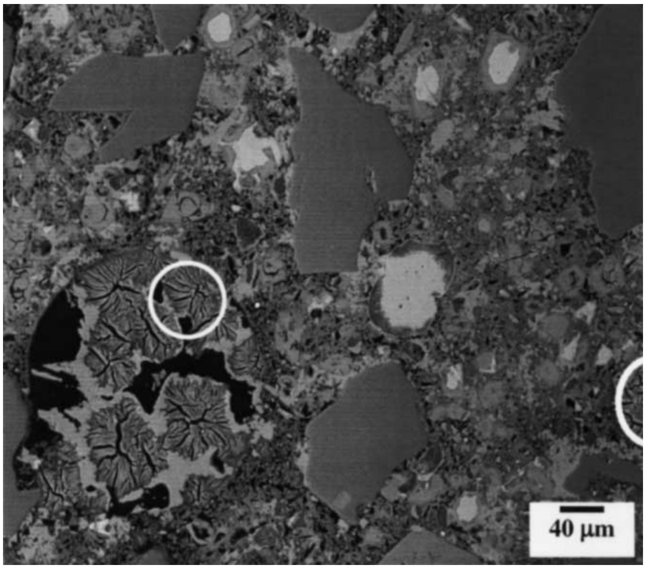

Fig. 11. BSE image of a 90°C/12 h cured mortar stored in the [P]KOH solution for 200 days. Large amounts of ettringite can be observed filling air voids and cavities (circles). No gap is present at the paste/aggregate interfaces.

analyses were plotted as atom ratios, and not as percentages of individual elements, to eliminate the effects of microporosity and water content of the C-S-H. The atom ratios of most interest are S/Ca and Al/Ca and results of microanalysis are therefore plotted as S/Ca versus Al/Ca.

After 1 day cure at 20°C, the microanalyses are spread over a large range of S/Ca and Al/Ca values (Fig. 12). As the microstructure shows (Fig. 7), the rims of inner C-S-H product are less than 1 μm thick, and the volume analysed (1 to 2 $\mu m^3$) therefore relates not only to C-S-H but also to other phases intermixed and adjacent to it. Microanalyses are consistent with intimate mixtures consisting largely of ettringite and an inner C-S-H containing small amounts of $SO_3$ and $Al_2O_3$. The minimum S/Ca atom ratios observed are higher than those previously reported for C-S-H formed at ordinary temperature, which likely shows that none of these microanalyses represent C-S-H free from ettringite. Where necessary, we shall use the term "C-S-H" for the phase and "C-S-H gel" for material that may be an intimate mixture of C-S-H and other phases.

In the mortar examined immediately after heating at 90°C, the degree of scatter in the S/Ca and Al/Ca atom ratios of the lighter inner C-S-H gel is less than that observed in the 20°C cured mortars (Fig. 12). This comes from the fact that thicker rims have formed at the higher temperature, with the result that the microanalyses give the composition of the inner C-S-H and not of that mixed with adjacent phases. High levels of sulphate and aluminate are present within the inner C-S-H gel following heat-curing. Previous studies indicate that sulphate is likely sorbed in the C-S-H layers and that most of the aluminium detected in the C-S-H substitutes for Si in the bridging sites of the silicate tetrahedra chains [13,32,33].

Fig. 13 shows the compositional changes in the lighter inner C-S-H gel during subsequent storage in water, at 90–100% RH or in a [P]KOH solution. Irrespective of the environment, all the heated mortars share the same trend as there is a release of sulphate from their lighter inner C-S-H gel over time. However, the rate at which sulphates are desorbed from the C-S-H depends on the post-heat treatment storage conditions. Within 200 days, the lighter C-S-H gel of the water-stored mortars gives the lowest S/Ca ratios whereas the 90–100% RH-stored mortars exhibit higher S/Ca ratios (Fig. 13). The sulphate release is even slower when the specimens are kept in the [P]KOH solution simulating the pore solution. The KOH stored mortars have only just started to expand (0.04%) although the specimens kept in water are reaching their ultimate degree of expansion (0.8%) and those stored at 90–100% RH give an intermediate expansion of 0.2% (Fig. 3). It appears that when the sulphates are released over a short period, expansion is higher.

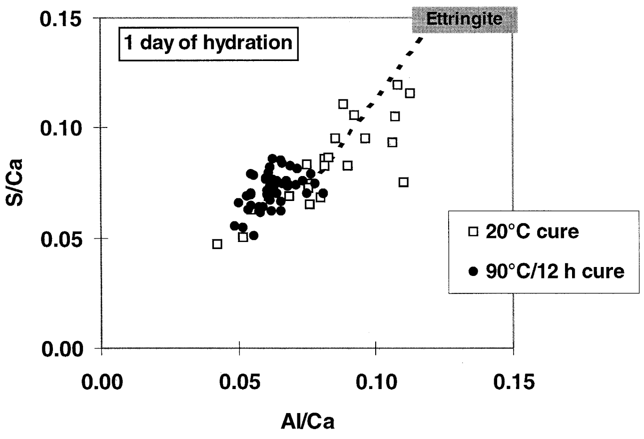

Fig. 12. S/Ca versus Al/Ca atom ratios for the inner C-S-H gel of the 20°C and 90°C cured mortars after 1 day of hydration. No subsequent storage.

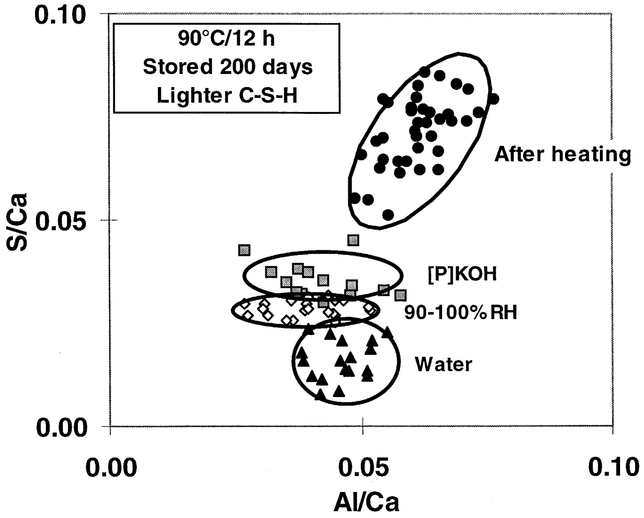

Fig. 13. S/Ca versus Al/Ca atom ratios for the lighter inner C-S-H gel of the 90°C cured mortars stored for 200 days in water, at 90–100% RH or in the KOH solution at $[P]_{KOH}$.

Fig. 14 and Table 3 show the effect of the KOH concentration of the storage solution on the composition of the lighter inner C-S-H gel. It is clear that the sulphate release from the lighter inner C-S-H gel is strongly dependent on the concentration of the KOH solution. The loss of

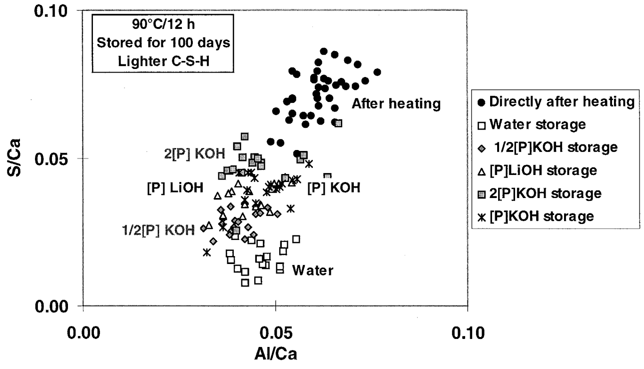

Fig. 14. S/Ca versus Al/Ca atom ratios for the lighter inner C-S-H gel of the 90°C cured mortars stored for 100 days in water, in KOH solutions of different KOH concentrations or in a LiOH solution.

Table 3
Mean Al/Ca and S/Ca atom ratios for the 90°C cured mortars stored in various storage mediums; directly after heating and after a 100-day storage

| | Al/Ca | | S/Ca | |
|---|---|---|---|---|
| Storage medium | Mean | S.D. | Mean | S.D. |
| Directly after heating (1 day old) | 0.061 | 0.007 | 0.070 | 0.003 |
| [2P]KOH | 0.046 | 0.008 | 0.047 | 0.007 |
| [P]KOH | 0.042 | 0.008 | 0.035 | 0.004 |
| [1/2P]KOH | 0.028 | 0.004 | 0.040 | 0.005 |
| [P]LiOH | 0.043 | 0.006 | 0.036 | 0.004 |
| Water | 0.046 | 0.005 | 0.016 | 0.005 |

sulphate at 100 days increases markedly with decreasing KOH concentration, and is closely similar for KOH and LiOH solutions of the same molar concentration.

## 4. Discussion on the expansion mechanism in view of these results

Upon subsequent storage sulphate is released from the lighter inner C-S-H gel at a rate that is affected by the hydroxide concentration of the pore fluid which, in turn, depends on the hydroxide concentration of the storage solution. The higher this concentration is, the lower is the rate of sulphate release and, with it, the expansion.

High KOH concentrations in the storage solution delay or even prevent the leaching of $K^+$ and $OH^-$ from the pore fluid, thus maintaining a high solubility of ettringite. The sulphate concentration of the pore fluid remains high. A sulphate concentration gradient exists between the $SO_4^{2-}$ incorporated within the lighter C-S-H gel and that in the pore solution. The driving force for the release of sulphate from the lighter C-S-H into the pore solution increases with this difference, and thus this depends on the formation of ettringite which itself depends on the alkalinity of the pore fluid.

Studies of the outer C-S-H product (i.e., that formed in space originally occupied by water as opposed to the inner C-S-H gel formed in situ from the clinker grains [34]) of the mortars described here show that, immediately after heating, some of the sulphate that it contains is sorbed on the C-S-H and that the rest is present in calcium monosulphoaluminate intermixed with the C-S-H on a submicrometre scale [13,30]. During the subsequent storage, the ettringite is initially formed in intimate admixture with the outer C-S-H gel from reaction between released sulphate and calcium monosulphoaluminate. Such growth of ettringite is likely to create crystallisation pressures because the ettringite crystals (which are not observable by SEM due to their small size — in the order of the fine outer C-S-H gel porosity) form in a limited space under high supersaturation levels. The calcium monosulphoaluminate is evenly distributed in the outer C-S-H gel and the paste expands, which causes it to become detached from aggregates creating gaps at the paste/aggregates interfaces. Thermodynamic considerations support the paste expansion mechanism [35]. The maximum pressure which can be exerted by crystal growth increases with the degree of supersaturation and decreases with increasing size of the pores in which the crystals grow.

The small ettringite crystals formed in the pores of the outer C-S-H gel dissolve and recrystallise through Ostwald ripening as larger ones in any larger spaces that are available (gaps, cavities and cracks).

No direct correspondence exists between the amount of ettringite semiquantified by XRD and the degree of expansion because most of the ettringite detected by XRD consists of the coarse ettringite observed in gaps, cavities and air voids and not that formed in situ in the outer C-S-H which is responsible for expansion.

## 5. Conclusions

- The experimental results presented here show that immediately after heat-curing no ettringite is detected by XRD but sulphate and aluminium enter calcium monosulphoaluminate and are also incorporated in the C-S-H gel. Sulphate is probably sorbed in the C-S-H gel while most of the aluminium in the C-S-H gel substitutes for Si.
- Sulphate is released from the C-S-H over time.
- Leaching of alkali hydroxide into the surrounding storage solution increases the rate at which sulphate is lost from the C-S-H.
- Limiting alkali hydroxide leaching therefore slows down sulphate release from the C-S-H and also retards the expansion process.
- These results lead to the conclusion that the mechanism of the expansion process is considerably more complex than acknowledged by many authors and cannot be ascribed simply to the formation of ettringite at paste/aggregate interfaces.
- They are consistent with a mechanism in which expansion occurs in the paste due to the growth of submicrometre ettringite crystals in situ in the outer C-S-H gel, from calcium monosulphoaluminate already present in the outer C-S-H gel and sorbed sulphate.

## Acknowledgments

The authors would like to thank Prof. H.F.W. Taylor for his pertinent comments.

## References

[1] S. Marusin, SEM studies of DEF in hardened concrete, Proc. Int. Conf. Cem. Microsc., 15th, 1993, pp. 289–299.

[2] D. Heinz, U. Ludwig, Delayed ettringite formation in heat-treated mortars and concretes, Concr. Precast. Plant Technol. 55 (11) (1989) 56–61.

[3] D. Heinz, U. Ludwig, Mechanism of secondary ettringite formation in mortars and concretes subjected to heat treatment, J.M. Scanlon (Ed.),

Concrete Durability, Am. Concr. Inst., SP 100-105, vol. 2, 1987, pp. 2059–2071 (Detroit).

[4] C.D. Lawrence, Technical report C/16, BCA, 1993.

[5] C.D. Lawrence, Delayed ettringite formation: An issue?Mater. Sci. Concr. IV, 1995, pp. 113–154.

[6] C. Famy, H.F.W. Taylor, Ettringite in the hydration of Portland cement concrete and its occurrence in mature concretes, Concr. Int., 2001 (in press).

[7] J. Stark, K. Bollmann, K. Seyfarth, Ettringit — Schadensverursacher, Schadensverstärker oder unbeteiligter Dritter (Ettringite — cause of damage, damage intensifier or uninvolved third party?), ZKG Int. 51 (5) (1998) 280–292.

[8] D.A. St. John, A discussion on the paper "Alkali metal sulphate — a factor common to both alkali aggregate reaction and sulphate attack on concrete", Cem. Concr. Res. 11 (5/6) (1981) 799.

[9] A.D. Jensen, Microscopy of old concrete structures, Proc. Int. Conf. Cem. Microsc., 18th, 1994, pp. 161–170.

[10] K. Pettifer, P.J. Nixon, Alkali metal sulfate — a factor common to both alkali aggregate reaction and sulphate attack on concrete, Cem. Concr. Res. 10 (2) (1980) 173–181.

[11] Y. Odler, Y. Chen, On the delayed expansion of heat cured portland cement pastes and concretes, Cem. Compos. 18 (1996) 181–185.

[12] M.C. Lewis, K.L. Scrivener, A microstructural and microanalytical study of heat cured mortars and delayed ettringite formation, Proc. Int. Congr. Chem. Cem., 10th, Gothenburg, vol. 4, 1997, pp. 409–416.

[13] C. Famy, Expansion of heat-cured mortars, PhD Thesis, Imperial College of Science, Technology and Medicine, University of London, 1999.

[14] R. Yang, C.D. Lawrence, C.J. Lynsdale, J.H. Sharp, Delayed ettringite formation in heat-cured Portland cement mortars, Cem. Concr. Res. 29 (1) (1999) 17–25.

[15] Z. Zang, Delayed ettringite formation in heat-cured cementitious systems, PhD Thesis, Purdue University, USA, 1999.

[16] M.C. Lewis, Heat curing and delayed ettringite formation in concretes, PhD Thesis, Imperial College of Science, Technology and Medicine, University of London, 1996.

[17] M.C. Lewis, K.L. Scrivener, S. Kelham, Heat curing and delayed ettringite formation, Proc. Mater. Res. Soc. Symp., 1994, pp. 67–76.

[18] S. Kelham, Effect of cement composition and hydration temperature on volume stability of mortar, H. Justness (Ed.), Proc. Int. Congr. Chem. Cem., 10th, Gothenburg, vol. 4, 1997, pp. 4iv060.

[19] S. Kelham, Presentation at the Cement and Concrete Science Conference, organised by SCI, Keele University, London, UK, 1999 (Sept).

[20] V. Johansen, N. Thaulow, U.H. Jackobsen, L. Palbol, Heat cured induced expansion, Proc. Beijing Int. Symp. Cem. Concr., 3rd, vol. 3, 1993, pp. 144–156.

[21] H.J. Kuzel, Initial hydration reactions and mechanisms of delayed ettringite formation in Portland cements, Cem. Concr. Compos. 18 (3) (1996) 195–203.

[22] K.L. Scrivener, The microstructure of concrete, J. Skalny (Ed.), Mater. Sci. Concr. I (1989) 127–161.

[23] K.L. Scrivener, W. Wieker, Advances in hydration at low, ambient and elevated temperature, Proc. Int. Congr. Chem. Cem., 9th, vol. 1, 1992, pp. 449–481.

[24] K.L. Scrivener, The effect of heat treatment on inner product C-S-H, Cem. Concr. Res. 22 (1992) 1224–1226.

[25] R.J. Detwiller, L.J. Powers-Couche, Ettringite — the sometimes host of destruction, B. Erlin (Ed.), Am. Concr. Inst., SP 177 (1999) 159–181.

[26] H.M. Sylla, Reactions in cement stone due to heat treatment, Beton 38 (11) (1988) 449–454.

[27] S. Diamond, Delayed ettringite formation — processes and problems, Cem. Concr. Compos. 18 (1996) 205–215.

[28] Y. Fu, J.J. Beaudoin, Mechanisms of delayed ettringite formation in portland cement systems, ACI Mater. J. 93-M36 (1996) 327–333.

[29] R.C. Mielenz, S.L. Marusin, W.G. Hime, Z.T. Jugovic, Investigation of prestressed concrete railway tie distress, Concr. Int. 17 (12) (1995) 62–68.

[30] C. Famy, K.L. Scrivener, A.R. Brough, A. Atkinson, E. Lachowski, Characterisation of C-S-H products in expansive and non-expansive heat cured mortars: An electron microscopy study, Proc. CANMET/ACI Conf. Durability of Concrete, Barcelona, 2000, pp. 385–402.

[31] J. Skalny, V. Johansen, N. Thaulow, A. Palomo, DEF: As a form of sulfate attack, Mater. Constr. 46 (244) (1996) 5–29.

[32] I.G. Richardson, A.R. Brough, R. Brydson, G.W. Groves, C.M. Dobson, Location of aluminium in substituted calcium silicate hydrate (C-S-H) gels as determined by $^{29}$Si and $^{27}$Al NMR and EELS, J. Am. Ceram. Soc. 76 (9) (1993) 2285–2288.

[33] C. Famy, K.L. Scrivener, A.R. Brough, A. Atkinson, E. Lachowski, Composition and structure of C-S-H formed in heat-cured Portland cement mortars: A microscopical and NMR study, in preparation.

[34] H.F.W. Taylor, Cement Chemistry, second ed., Thomas Telford Publishing, London, 1997.

[35] G.W. Scherer, Crystallisation in pores, Cem. Concr. Res. 29 (8) (1999) 1347–1358.