Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 1341–1356

CEMENT AND CONCRETE RESEARCH

The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature
Part II: Microstructural and microchemical investigations

T. Ramlochan[a], M.D.A. Thomas[b], R.D. Hooton[a]

[a]*Department of Civil Engineering, University of Toronto, 35 St. George Street, Toronto, ON, Canada*
[b]*Department of Civil Engineering, University of New Brunswick, Fredericton, NB, Canada*

Received 15 July 2003; accepted 17 December 2003

Abstract

The microstructural and microchemical development of heat-cured Portland cement mortars containing silica fume, metakaolin, blast-furnace slag, and fly ash were analysed using pore solution analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX). Incorporation of these materials into the mixture modifies the composition of the C-S-H gel, the quantities of the hydration products, and the microstructure. Ettringite was formed during moist storage in all specimens, but was not accompanied by expansion where a sufficient amount of metakaolin, blast-furnace slag, or a suitable fly ash replaced a proportion of the Portland cement; replacement with silica fume was not as effective at eliminating expansion. The different behaviour of silica fume from the other supplementary cementing materials is believed to reflect a difference in the way ettringite is formed in the presence of Al_2O_3-bearing mineral admixtures.

Keywords: Ettringite; Expansion; Monosulphate; Blended cement; Heat curing

---

1. Introduction

Mortars and concretes that have been cured at high temperatures (typically above ~ 70 °C) may in some instances undergo significant expansion, if subsequently exposed to moisture, by a process referred to as delayed ettringite formation (DEF). In a previous paper [1] it was demonstrated that some pozzolans or slag, when used as a partial replacement for a cement that exhibits expansive behaviour, were beneficial in reducing or even suppressing expansion in heat-cured mortars that were stored in limewater for as long as 4 years. Materials that contain large amounts of reactive Al_2O_3, such as metakaolin, fly ash, and blast-furnace slag, were found to be the most effective at controlling long-term expansion, whereas silica fume appeared to only delay significant expansion. This paper reports on work performed as part of a larger study [2] that attempts to elucidate the role that these mineral admixtures may have in suppressing expansion by looking at the formation and composition of the hydration products and crystalline products present in heat-cured mortars containing pozzolans or slag, at early and later ages. The evolution of the chemical composition of the pore fluids is also reported.

Kalousek and Adams [3] were the first to describe the chemistry of cement systems hydrated at high temperatures. They found that in cement pastes hydrated at 70 to 100 °C the ettringite that was formed initially was replaced by monosulphate upon heating, and that these phases never accounted for more than one half of the total sulphate. They concluded that some of the Al and S were incorporated into the hydration products (i.e., the C-S-H gel) and this increased with temperature, though it also occurred to a lesser extent at normal temperatures. Subsequent work by other investigators has confirmed that at elevated temperature the formation of ettringite is inhibited, particularly in the presence of alkalis, to the extent that a considerable amount of sulphate enters the C-S-H that is formed [4]. Some sulphate also remains in the pore fluid following heat curing. Sulphate ion concentrations as high as ~ 200 mM have been reported [5–8]. However, mass balance calculations suggest that the sulphate remaining in the pore fluid

---

* Corresponding author. Tel.:+1-416-978-5912; fax:+1-416-978-7046.
E-mail address: d.hooton@utoronto.ca (R.D. Hooton).

0008-8846/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2003.12.026

at the end of the heat cure is probably much less important with respect to DEF than the sulphate entering the C-S-H [9].

A number of researchers have examined the C-S-H formed at elevated temperature in the scanning electron microscope (SEM) with energy-dispersive X-ray analysis (EDX). X-ray microanalyses of the inner product of cement grains in pastes or mortars cured at 70 to 100 °C typically give Al/Ca molar ratios of ∼ 0.04–0.06 and S/Ca molar ratios as high as ∼ 0.10 within 24 h of hydration [9–12]. These Al/Ca ratios are similar to those reported for pastes cured at 20 °C [13], but the S/Ca ratios are much higher than those of ∼ 0.01–0.04 commonly found in pastes cured at ordinary temperatures [14,15]. Most of the Al^{3+} present in the C-S-H appears to be primarily substituted for Si^{4+} [8,16], whereas the sulphate incorporated into the C-S-H has been described as adsorbed [17]. With moist storage, sulphate can be desorbed from the C-S-H. The mean S/Ca ratio of the C-S-H formed during the heat curing typically decreases to values of about 0.02–0.03 during storage [8,11,12], which is similar to that of the C-S-H that forms later. The Al/Ca ratio of the C-S-H decreases only slightly during storage, to values of about 0.04 [8,11,12].

The release of sulphate from the C-S-H at later ages can result in the formation of ettringite in the hardened material. X-ray diffraction (XRD) analyses typically show the formation of previously undetected ettringite within days of moist storage. Results of semiquantitative determinations by XRD or thermal methods show no general relationship between expansion and the amount of ettringite formed [8,11,18,19]. While a complete explanation of the DEF mechanism is not yet available, microstructural and microanalytical evidence [8] suggests that in expansive mortars, submicrometer-sized ettringite crystals subsequently form in the paste, most likely from reaction of sulphate with monosulphate that is intimately mixed with the C-S-H in the outer product at the end of the heat treatment, leading to an expansion of the paste.

2. Experimental

Mortars containing various levels of pozzolans or slag as a partial cement replacement were heat cured at temperatures up to 95 °C and subsequently stored in lime-saturated water at ambient temperature. The details of the mixing and curing procedures are given in a previous paper [1]. The chemical compositions of the cementitious materials used are given in Table 1.

Table 1
Chemical compositions of cement, pozzolans, and slag used in this study

	Type III cement	Silica Fume	Metakaolin	Blast-furnace slag	Class F fly ash	Class C fly ash
SiO_2	20.1	95.52	52.06	35.55	50.91	36.08
Al_2O_3	5.5	0.15	45.29	9.42	25.41	17.88
TiO_2	0.27	0.01	1.64	0.83	1.13	1.44
P_2O_5	0.07	0.11	0.1	0	0.51	1.63
Fe_2O_3	2.08	0.04	0.6	0.48	13.53	6.45
CaO	63.6	0.3	0.05	38.02	2.79	26.04
SrO	0.05	0.01	0.1	0.01	0.11	0.46
MgO	1.5	0.15	0	11.01	0.88	4.93
Mn_2O_3	0.05	0.01	0.02	0.85	0.04	0.02
Na_2O	0.1	0.1	0.21	0.4	0.65	1.62
K_2O	1.3	0.75	0.16	0.44	1.97	0.38
LSO_3	4.91	0.22	0	3.50[a]	0.85	1.74
LOI	0.63	2.11	0.51	$(-1.69)^{750\ °C}$	1.71	0.28
Total	100.16	99.48	100.74	100.51	100.47	98.92[b]
Na_2Oe	0.96	0.59	0.32	0.69	1.95	1.87
Na_2O soluble	0.08					
K_2O soluble	1.17					
FCaO	0.95					
SSB cm^2/g	5300					

[a] Mostly present as sulfide, but expressed as SO_3.

[b] Qualitative analysis by XRF showed the presence of barium and nickel.

XRD patterns were obtained from powdered mortar samples using monochromatized CuKα radiation having a wavelength of 1.54051 Å. The powder samples were prepared by lightly grinding nondried mortars with a porcelain mortar and pestle, being careful to minimize the amount of quartz aggregate that was crushed, and then passing the sample through a 90-μm sieve to remove most of the quartz. The powdered mortar samples were then intermixed with 10 wt.% of anatase (TiO_2) as an internal standard and ground in an agate mortar and pestle, with anhydrous ethanol as a grinding agent, using a very light pressure to minimize damage to the crystalline phases.

Pore fluids were extracted from mortars under high pressure, using a method and apparatus similar to that first described by Longuet et al. [20] and later by Barneyback and Diamond [21], to investigate how the concentrations of the ionic species in solution were affected by heat treatment and by the incorporation of pozzolans and slag. The hydroxyl ion concentration of the pore fluid was determined by potentiometric titration with 0.05 M H_2SO_4. The concentrations of other ionic species were determined by inductively coupled plasma atomic emission optical spectroscopy (ICP-AEOS). Pore solutions were extracted at various ages: at 20 min after mixing; at 4 h, directly before the application of heat; as soon as practicable following the heat treatment; and at later ages after storage in limewater.

Microstructural and microanalytical examination of mortars was performed in a scanning electron microscope fitted with an energy dispersive X-ray analyser, which was calibrated for the requisite elements with standards of suitable pure phases. X-ray microanalyses were performed at an accelerating voltage of 20 keV, with a specimen current maintained at approximately 0.9 nA. Quantitative elemental analysis was done on polished specimens. ZAF matrix corrections (three iterations) were applied to microanalyses.

Analyses were made for Na, Mg, Al, Si, S, P, K, Ca, Ti, Mn, and Fe. Oxygen was calculated by stoichiometry based on the most common oxide formulae. The microanalyses were not normalized.

Polished specimens were prepared from mortar bar samples taken immediately following heat curing and at later ages after storage in limewater. At early ages (e.g., 1 or 3 days) an attempt was made to stop the hydration of the mortar samples by cooling them rapidly for 1 h in a liquid nitrogen bath and then placing them in a vacuum desiccator maintained at − 20 °C to remove the evaporable water from the mortars. While this method of stopping hydration may not be perfect, it was thought to be sufficient for these purposes. At later ages it was not necessary to stop hydration instantaneously, so the initial cooling in the liquid nitrogen bath was not used. Instead, the samples were placed in a vacuum desiccator at room temperature above silica gel and soda lime for 2–3 days and then transferred to a vacuum desiccator maintained at − 20 °C to remove the remaining evaporable water. Once sufficiently dried, the samples were vacuum impregnated with a room-temperature-setting, low-viscosity epoxy resin, then polished and carbon coated.

3. Results

3.1. Expansive behaviour

Fig. 1 shows the expansion of mortars that were investigated in this study, which were initially cured at 95 °C and subsequently stored in limewater at room temperature. The Portland cement mortar expanded by more than 2.5% at 1 year. The 8% silica fume blended cement mortar also expanded significantly, but the onset of expansion was delayed, the rate of expansion was slower, and the ultimate expansion was much less (∼ 1.1%). No appreciable expansion (i.e., not greater than ∼ 0.04%) was observed with mixtures containing 8% metakaolin, 25% blast-furnace slag, or 25% of either the Class F fly ash or Class C fly ash. The Portland cement mortar did not undergo expansion when continuously cured at room temperature.

3.2. Pore solution analysis

Table 2 gives the concentrations of SO_4^{2-}, Na^+, K^+, Ca^{2+}, and OH^- ions in the pore fluid of the Type III Portland cement mortar before (extracted at 20 min, 2 h, and 4 h) and after (extracted at 24 h) curing at 95 °C and at room temperature. The concentrations of the aluminate and silicate ionic species were also determined, but were all very low (e.g., 1 mM) and are not reported.

Upon mixing, the pore fluid was dominated by SO_4^{2-}, K^+, and OH^- derived mainly from the dissolution of the alkali sulphates in the cement. The Na^+ concentration was not particularly high as most of the alkalis in the cement occurred as K_2O. The composition of the pore fluid changed very little over the first 4 h (i.e., before the heat treatment was applied). With the Portland cement mortar that was continuously cured at room temperature, the sulphate ion concentration decreased markedly between 4 and 24 h to ∼ 12 mM. Accordingly, the Ca^{2+} ion concentration decreased during this time and the OH^- ion concentration increased. When curing was done at 95 °C the sulphate concentration remained high, almost 20 times greater (213 mM) than in the room-temperature-cured mortar at 24 h. Consequently, the OH^- ion concentration was suppressed following heat curing. The high level of sulphate remaining in the pore fluid during the heat curing is attributed to an increase in the solubility of ettringite, which has been reported to increase markedly with temper-

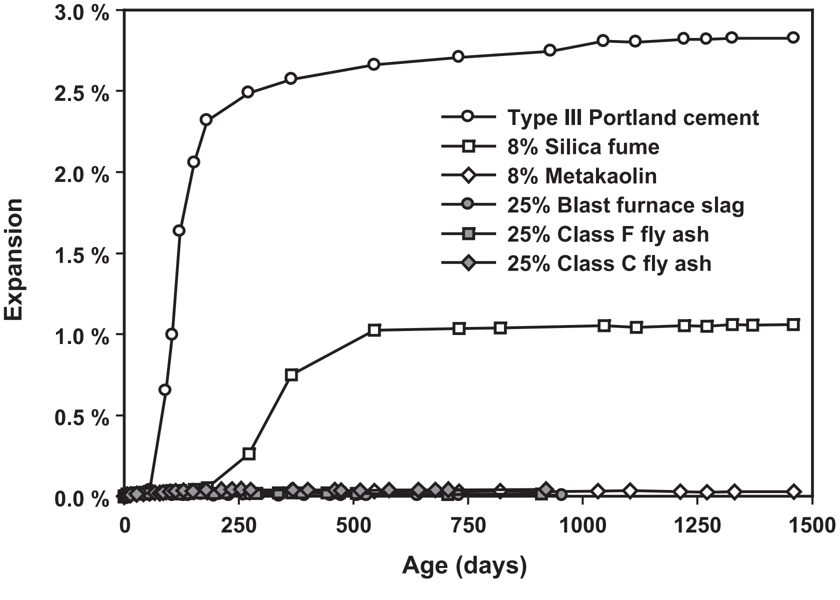

Fig. 1. Expansion of standard mortar bars containing pozzolans or slag cured at 95 °C and subsequently stored in limewater at ambient temperature.

Table 2
Concentration (mM) of ionic species in pore fluids extracted from Portland cement mortars cured at 23 or 95 °C, and from blended cement mortars cured at 95 °C

Mixture	Age	$[Ca^{2+}]$	$[K^+]$	$[Na^+]$	$[SO_4^{2-}]$	$[OH^-]$
Type III only (23 °C)	20 min	18.0	351	36.7	170	131
	2 h	18.3	382	37.4	163	181
	4 h	17.9	395	39.6	175	167
	24 h	0.9	654	47.0	12	711
Type III only (95 °C)	24 h	4.8	562	51.7	213	243
8% Silica fume	24 h	9.5	385	42.7	172	122
8% Metakaolin	24 h	2.3	433	50.4	106	285
25% Blast-furnace slag	24 h	3.0	467	83.5	163	238
25% Class F fly ash	24 h	3.5	526	99.1	148	208
25% Class C fly ash	24 h	3.5	490	266	185	243

ature [7]. It is important to note that, accounting for changes in the volume of pore fluid during the heat curing, the sulphate present in the pore fluid directly after the heat treatment amounted to at most ~ 10% of the total SO_3 in the system. With this in mind, the pore solution is likely not the primary store for the sulphate that later leads to the formation of ettringite.

The concentrations of ions in the pore fluids extracted from mortars containing pozzolans and slag immediately after heat curing at 95 °C are also given in Table 2. In all cases the sulphate ion concentrations were lower in the blended cement mortars compared to the Portland cement mortar after curing at 95 °C, but they were all still significantly higher than that of the room-temperature-cured mortar. Of the blended cement mixtures investigated, the 8% metakaolin mortar had the lowest SO_4^{2-} ion concentration (106 mM) following heat curing, much lower than might be expected from replacing 8% of the cement with metakaolin. The 25% Class C fly ash mortar had the highest SO_4^{2-} ion concentration (185 mM), and unlike the other mixtures investigated there appeared to be a contribution to the level of sulphate in the pore fluid form the mineral admixture. The Na^+ ion concentration was also notably higher with the 25% Class C fly ash mortar, which again is likely due to a contribution from the Class C fly ash.

When the mortars were immersed in limewater, the concentration of K^+ ions in the pore fluid decreased to ~ 10 mM with both the Portland cement mortars and the blended cement mortars, and in all cases the SO_4^{2-} ion concentrations decreased to trace levels (< 1 mM). The OH^- ion concentration also decreased during storage, but ultimately stabilized at ~ 50 mM in all of the mortars, balanced primarily by Ca^{2+}. Analysis of the limewater storage solution[1] showed a buildup of K^+ along with some Na^+, but only trace levels of SO_4^{2-}. This would suggest that substantially all of the alkalis were leached from the pore solution, but that the sulphate was not. The rate at which the alkalis were leached from the pore fluid was not the same between the different mixtures. The rate of leaching was greater with the Portland cement, fly ash, and slag mortars, and was slower with the silica fume and metakaolin mortars. For comparison, Figs. 2 and 3 show the composition of the pore fluid in the 95 °C-cured Portland cement mortar and 8% silica fume mortar over time. The difference in the rate of leaching is most likely due to differences in permeability, or more correctly diffusivity, between the mortars. In the case of the 8% silica fume mortar, this may partly explain why the onset of expansion was delayed and the rate of expansion was slower.

3.3. XRD analysis

The development of crystalline phases was studied on mortars using XRD immediately following heat curing and at later ages after storage in limewater. The relative amount of crystalline ettringite in each mortar was determined semiquantitatively by XRD using the reference intensity ratio method with anatase as an internal standard. A correction was made for the relative amount of quartz aggregate remaining in the sample after grinding.

Figs. 4 and 5 show the evolution of the crystalline phases detected by XRD for the Portland cement mortars cured at room temperature and at 95 °C, respectively. In the 95 °C mortar the primary sulphoaluminate phase detected at early age was monosulphate, identified by a broad peak at 8.93 Å. Ettringite was not detected in the 95 °C heat-cured mortar immediately following the heat treatment. In the room-temperature-cured mortar, ettringite was the primary sulphoaluminate phase detected at early ages, identified by its basal peak at 9.75 Å, and other peaks, indicating that some if not all of the ettringite was well crystallized. Monosulphate was not detected by XRD at early ages in the room-temperature-cured mortar, though this does not necessarily indicate its absence, as much of the monosulphate at early ages is likely poorly crystalline and not detectable by XRD. An appreciable amount of a hydrogarnet-type phase approximating to $C_3AS_{0.5}H_5$ was found in the 95 °C-cured mortar, but not in the room-temperature-cured mortar.

During storage in limewater, a small and somewhat broad monosulphate peak was detected in the pattern of the room-temperature-cured Portland cement mortar. The ettringite that was present at early ages persisted and there was even some increase in the amount of ettringite detected at 580 days. In the 95 °C heat-cured Portland cement mortar the monosulphate peak increased slightly at 90 days, but then disappeared at later ages. Ettringite was detected at 90 days and beyond, the amount increasing significantly over time. Table 3 gives the relative amounts of ettringite present in the room-temperature-cured and 95 °C-cured mortars deter-

---

[1] The limewater storage solution was replaced regularly with fresh solution if the concentration of K^+ and Na^+ reached ~ 10 mM.

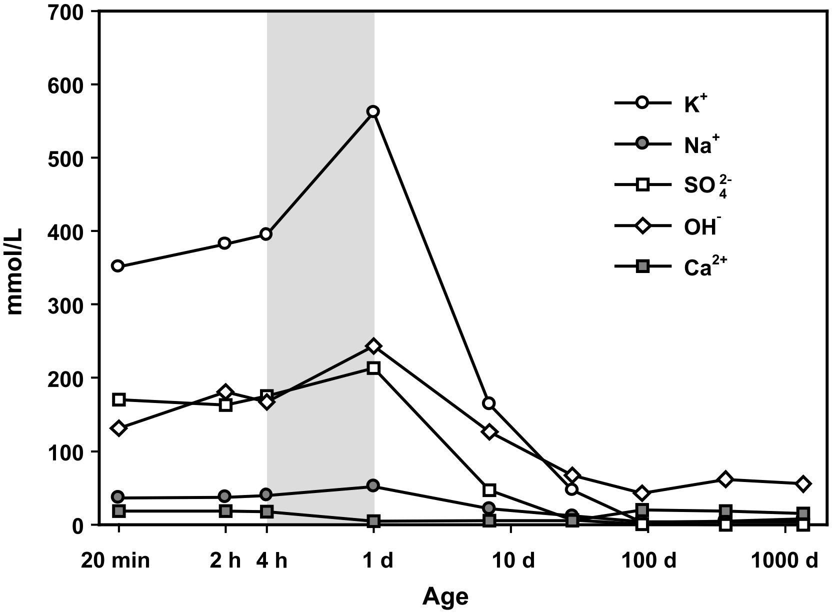

Fig. 2. Evolution of ionic species in the pore fluid of the Portland cement mortar cured at 95 °C. Note that the horizontal scale is logarithmic. The shaded region is the heat-curing period. The mortar bars were stored in limewater at ambient temperature beyond 1 day.

mined semiquantitatively by XRD. Interestingly, after ~ 600 days of storage in limewater, the amount of ettringite in the room-temperature-cured and 95 °C-cured mortars was similar. With the 95 °C Portland cement mortar, the formation of ettringite during storage was accompanied by expansion, but not with the room-temperature-cured mortar. The hydrogarnet-type phase present after heat curing at 95 °C persisted over time and there was no indication that any more was formed during subsequent storage at ambient temperature. In both the room-temperature-cured and 95 °C-cured Portland cement mortars some monocarbonate formed at later ages.

As with the Portland cement mortar, immediately following heat curing at 95 °C, ettringite was not detected in any of the mortars containing pozzolans or slag. Monosulphate was the primary sulphoaluminate phase present in all of the blended cement mortars. The intensity of the monosulphate peaks varied between the blended cement mortars, but in all cases was greater in the blended cement mortars than the Portland cement mortar. The monosulphate peak

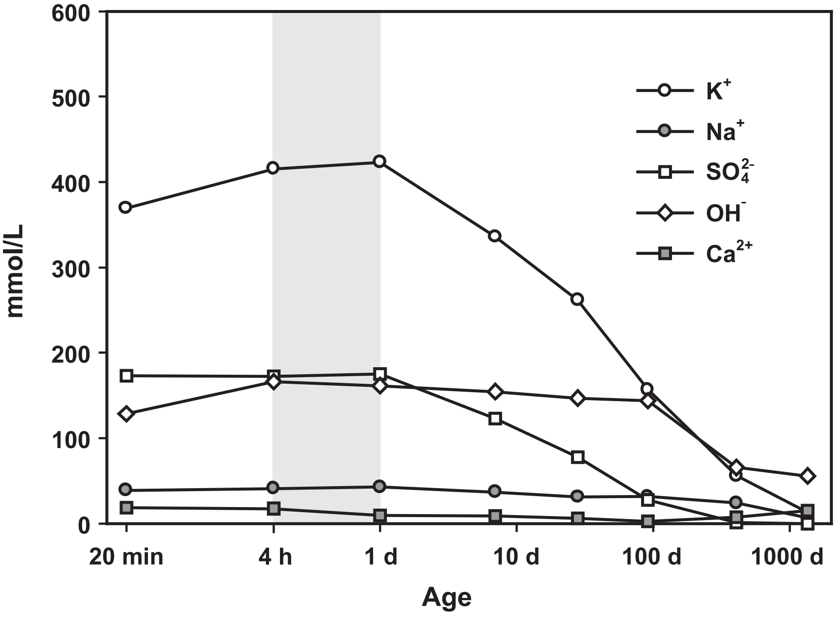

Fig. 3. Evolution of ionic species in the pore fluid of the 8% silica fume mortar cured at 95 °C. Note that the horizontal scale is logarithmic. The shaded region is the heat-curing period. The mortar bars were stored in limewater at ambient temperature beyond 1 day.

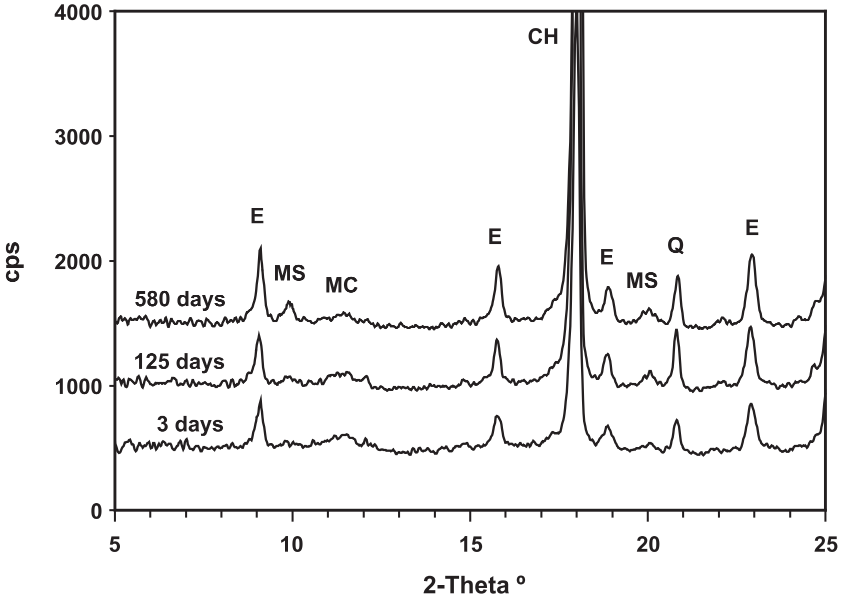

Fig. 4. XRD diffractograms of the room-temperature-cured Portland cement mortar. E, ettringite; MS, monosulphate; MC, monocarbonate; CH, calcium hydroxide; Q, quartz.

was strongest in the mortars containing 8% metakaolin or 25% Class F fly ash, which may indicate that more monosulphate was present in these mortars following the heat curing, or that the monosulphate present was more crystalline. In all of the blended cement mortars the monosulphate peaks decreased over time. In the silica fume mortar the monosulphate peak disappeared beyond 530 days, whereas in the metakaolin and Class F fly ash mortars, and to a lesser extent the Class C fly ash and slag mortars, there were still notable monosulphate peaks after as many as 1350 days of storage in limewater.

Figs. 6 and 7 show the evolution of the crystalline phases in the 8% silica fume mortar and the 8% metakaolin mortar, respectively. As with the heat-cured Portland cement mortar, during subsequent storage at ambient temperature, a significant amount of ettringite formed in these mortars, as well as those containing fly ash or slag (not shown). The relative amount of ettringite detected by XRD in all of the blended cement mortars is given in Table 3. With the exception of the 95 °C-cured 8% silica fume mortar, the formation of ettringite during storage was not accompanied by expansion with the blended cement mortar mixtures investigated.

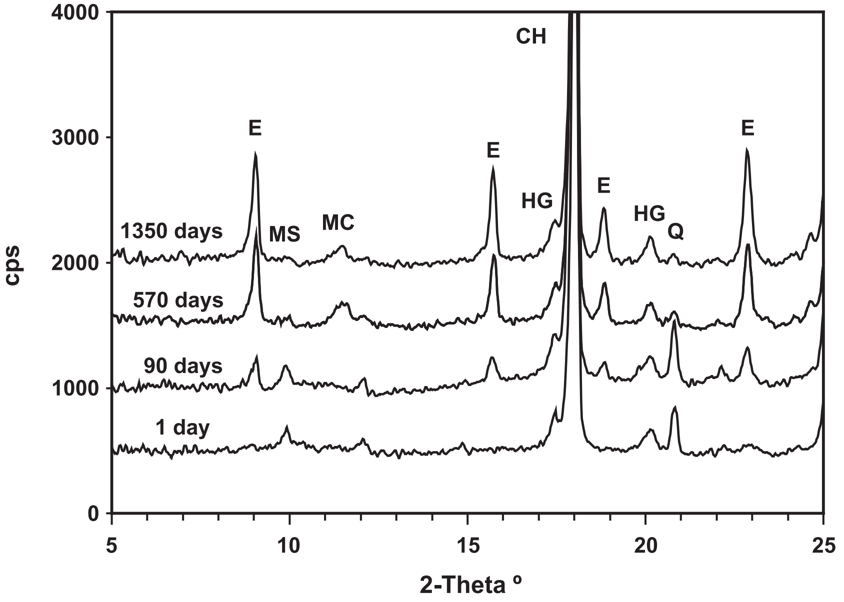

Fig. 5. XRD diffractograms of the 95 °C heat-cured Portland cement mortar. E, ettringite; MS, monosulphate; MC, monocarbonate; CH, calcium hydroxide; Q, quartz, HG, hydrogarnet.

Table 3
Relative amount of ettringite in Portland cement mortars cured at 23 or 95 °C, and from blended cement mortars cured at 95 °C determined semiquantitatively by XRD

Mixture	Age (days)	Relative amount of ettringite (%)
Type III only (23 °C)	3	48
	125	52
	580	81
Type III only (95 °C)	90	39
	570	77
	1350	100
8% Silica fume	91	20
	530	60
	1350	92
8% Metakaolin	90	18
	560	51
	1350	69
25% Blast-furnace slag	90	19
	560	49
	1140	50
25% Class F fly ash	90	30
	550	36
	1050	48
25% Class C fly ash	90	38
	510	61
	1060	72

The values are normalized by the amount of ettringite detected in the 95 °C Portland cement mortar at 1350 days.

A hydrogarnet-type phase was detected in the 95 °C heat-cured metakaolin, slag, and fly ash mortars, but was not identified in the 95 °C heat-cured silica fume mortar. The amount present immediately after heat curing did not change during storage. In the blast-furnace slag mortar a small amount of a hydrotalcite-type phase (approximating $M_{4.5}AH_x$) was identified immediately after heat curing, and the amount appeared to increase slightly over time. Monocarbonate was detected in all of the blended cement mortars at later ages; the amount was greatest in the metakaolin mortar.

3.4. SEM and EDX analyses

3.4.1. Portland cement mortars

Microstructural and microanalytical investigations were performed in the SEM with EDX on specimens obtained immediately after heat curing and at later ages after storage in limewater. Both the inner and outer hydration products, differentiated as material that forms in the space initially occupied by the cement grains and by the water, respectively, were analyzed. For statistical accuracy, approximately 30–50 EDX microanalyses were taken of the inner product, or inner C-S-H, of different alite particles from each specimen. Microanalyses were taken at locations where the inner C-S-H was sufficiently thick to minimize the contribution of adjacent phases. Microanalyses with totals greater than 80% were considered to contain unacceptable amounts of anhydrous phases and were excluded. Owing to its greater inhomogeneity, as many as 150 microanalyses were made of the outer product from each specimen. Most of the microanalyses were taken at locations that were considered to be primarily C-S-H, though it should be appreciated that the excited volume for each microanalysis may be as much as 3 μm in the lateral direction, with a penetration of up to 4 μm, and may contain appreciable amounts of other phases. Additional

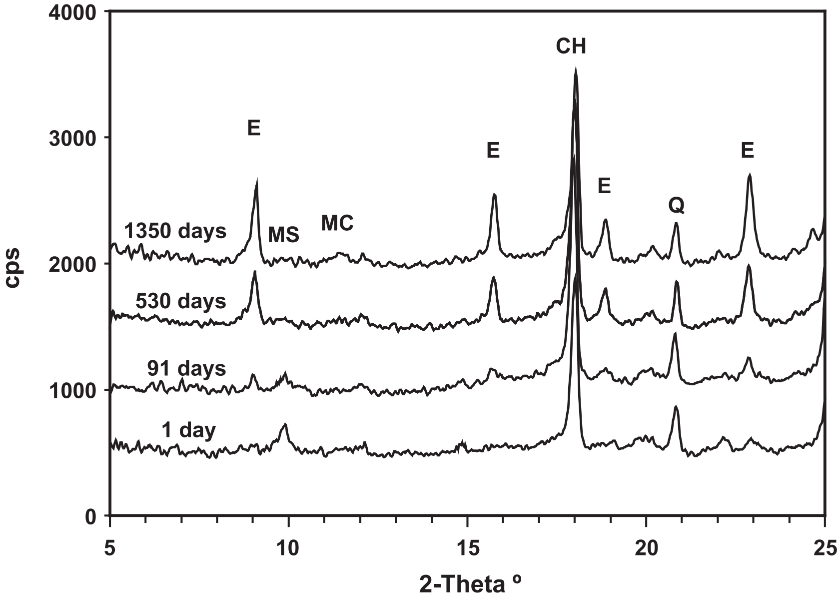

Fig. 6. XRD diffractograms of the 95 °C heat-cured 8% silica fume mortar. MS, monosulphate; MC, monocarbonate; CH, calcium hydroxide; Q, quartz, HG, hydrogarnet.

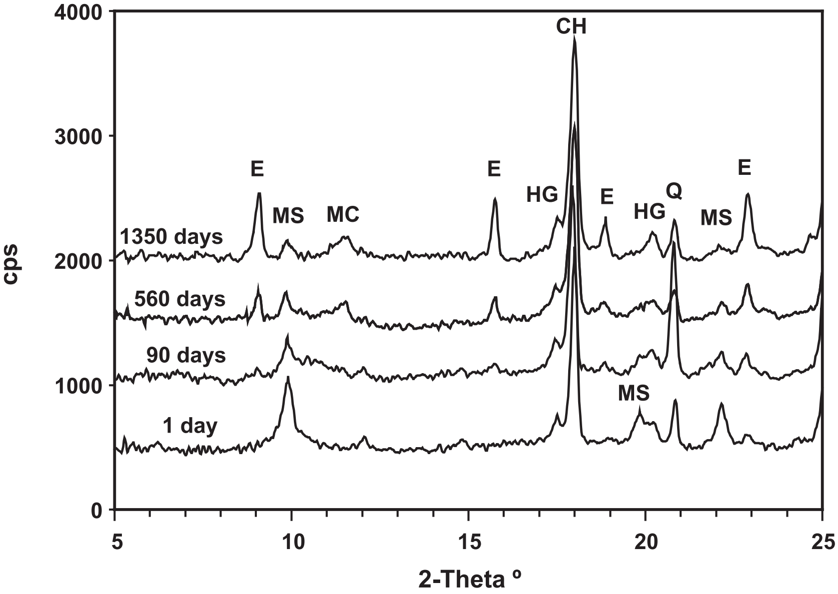

Fig. 7. XRD diffractograms of the 95 °C heat-cured 8% metakaolin mortar. MS, monosulphate; MC, monocarbonate; CH, calcium hydroxide; Q, quartz, HG, hydrogarnet.

details of the analysis procedures can be found elsewhere [2].

Following heat curing at 95 °C there were dense rims of inner C-S-H, which were ~ 5 μm thick, around the partially reacted alite particles in the Portland cement mortar. These rims were relatively uniform in thickness and grey level by backscattered-electron imaging (BEI), and they were brighter grey (i.e., greater backscatter coefficient) than those typically found when curing was done at lower temperatures. The latter has been attributed to a lower nanoporosity of the inner C-S-H formed at elevated temperature [10], though there were also compositional differences that may have an influence on the backscatter coefficient.

Microanalyses of the inner C-S-H directly after heat curing at 95 °C gave a mean S/Ca molar ratio of 0.079, a mean Al/Ca molar ratio of 0.054, and a mean Ca/Si molar ratio of 2.13. For comparison, the inner C-S-H in a companion mortar continuously cured at room temperature for 3 days had mean ratios of 0.044, 0.056, and 1.97, respectively. Considerably more sulphate was incorporated in the inner C-S-H with the mortar cured at 95 °C. The difference in the Ca/Si ratio between the two specimens would suggest that the most likely mechanism for charge balance of the excess sulphate incorporated in the inner C-S-H formed at elevated temperature is incorporation of additional Ca^{2+}. An estimate of the probable amount of sulphate incorporated in the C-S-H during the heat curing suggests that it could be more than fivefold of that remaining in the pore fluid.

Microanalyses of the outer product are hardly ever of single phases and likely contain small amounts of other phases, such as calcium hydroxide, ettringite, monosulphate, etc., which are intermixed with the C-S-H gel. Interpreting these data is not straightforward. The absolute values of individual microanalyses (i.e., at.% or single atomic ratios) are less useful than are plots of the atomic ratios. Figs. 8 and 9 show the microanalyses taken of the outer product in the Portland cement mortar cured at room temperature and at 95 °C at early age, plotted as S/Ca versus Al/Ca molar ratios. In general, each plot is dominated by a cluster of points representing the microanalyses where the sample volume was mostly C-S-H. There was a notable difference in the distribution of the microanalyses between the mortar cured at room temperature and that cured at 95 °C. With the former, the microanalyses stretch along the AFt line indicating the presence of ettringite on a fine scale

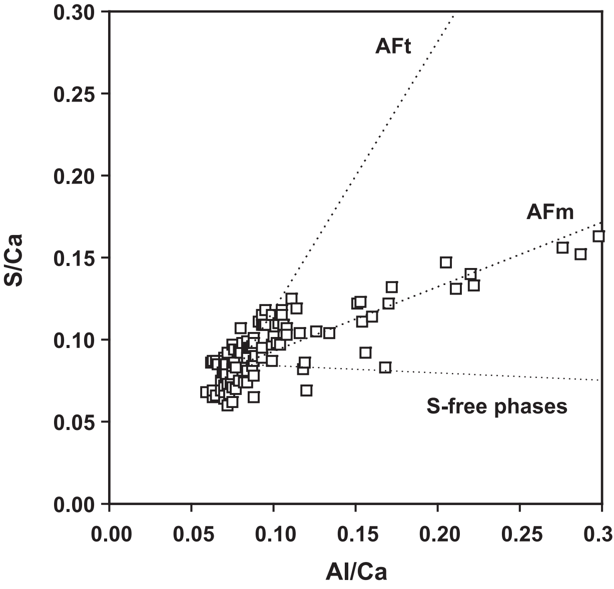

Fig. 8. EDX microanalyses of the outer product in the room-temperature-cured Portland cement mortar at 3 days.

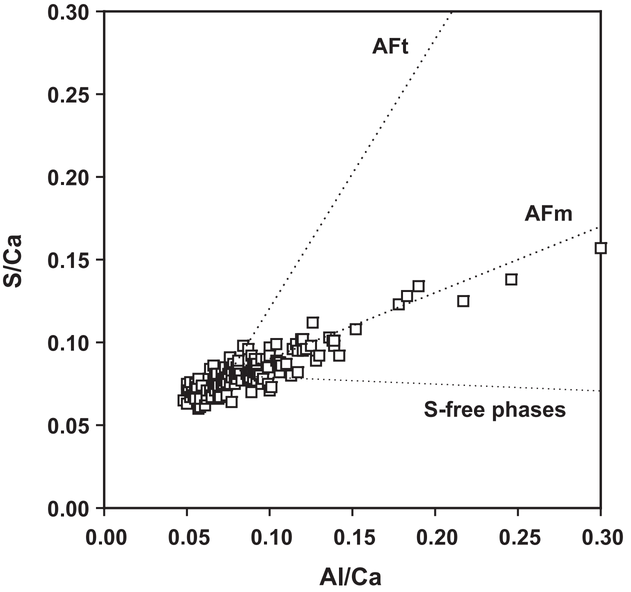

Fig. 9. EDX microanalyses of the outer product in the Portland cement mortar directly after (1 day) heat curing at 95 °C.

with the C-S-H in the outer product. With the latter, the microanalyses stretch along the AFm line indicating that the outer C-S-H was mixed with monosulphate on a fine scale. This is consistent with the results of XRD analyses of these mortars. Furthermore, small acicular crystals of what appeared to be ettringite, only a few micrometers in length, were observed by BEI randomly scattered throughout the paste of a fracture surface of the room-temperature-cured mortar, but not the mortar cured at 95 °C. Together, this would indicate that ettringite was not present after heat curing at 95 °C. Monosulphate, which was not detected in the room-temperature-cured mortar by XRD at early age, was observed by BEI of polished sections in both the room-temperature-cured mortar and the 95 °C-cured mortar, though with the latter there appeared to be significantly more present. Some of the monosulphate was deposited in small cavities or in the hollow shells remaining from the complete dissolution of very small cement grains, but much of the monosulphate observed were small platy lumps occluded by the fibrillar C-S-H in the outer product. These deposits of monosulphate were relatively large (often several micrometers in size) and their microanalyses typically plot along the AFm line away from the main cluster of points.

After 580 days of storage in limewater, the mean S/Ca, Al/Ca, and Ca/Si molar ratios of the inner C-S-H in the room-temperature-cured mortar, which was formed at early age, were 0.032, 0.050, and 1.94, respectively. The values were not considerably different from those found at 3 days. The microanalyses of the outer product remained largely unchanged after storage and still indicated that ettringite was present on a fine scale in the outer product. At this age, larger crystals of ettringite were also readily found in many voids.

In contrast, the mean S/Ca and Ca/Si molar ratios of the inner C-S-H that formed at elevated temperature in the 95 °C-cured mortar decreased significantly during storage, to 0.016 and 1.83, respectively, at 570 days. This would indicate that most of the sulphate incorporated in the inner C-S-H during the initial heat treatment was released during moist storage at ambient temperature. The mechanism by which sulphate is incorporated into the C-S-H is not clear, but is consistent with an adsorption phenomenon, since it is so readily removed during moist storage. The mean Al/Ca molar ratio also decreased during storage, though not extensively, to 0.042 at 570 days, suggesting that much of the Al present in the inner C-S-H was strongly bound and probably substituted.

Microanalyses of the outer product also showed a general decrease in sulphate content over time. This in part may be due to a release of sulphate from the C-S-H gel in the outer product, which itself probably takes up sulphate during the heat treatment, but is most likely due to a consumption of the monosulphate that was finely mixed with the outer C-S-H after the heat curing. Figs. 10 and 11 show the microanalyses of the outer product in the 95 °C-cured mortar after 200 days of storage and 1350 days, respectively. After 200 days, many of the microanalyses related to ettringite being present on a fine scale with the C-S-H gel in the outer product, though most still related to monosulphate. After 1350 days of storage, there was no indication that either monosulphate or ettringite was present on a fine scale with the C-S-H in the outer product. This would suggest that during moist storage ettringite initially forms on a fine scale intermixed with the outer C-S-H, most likely from a reaction of the sulphate released from the C-S-H with the monosulphate that is intermixed on a fine scale with the outer C-

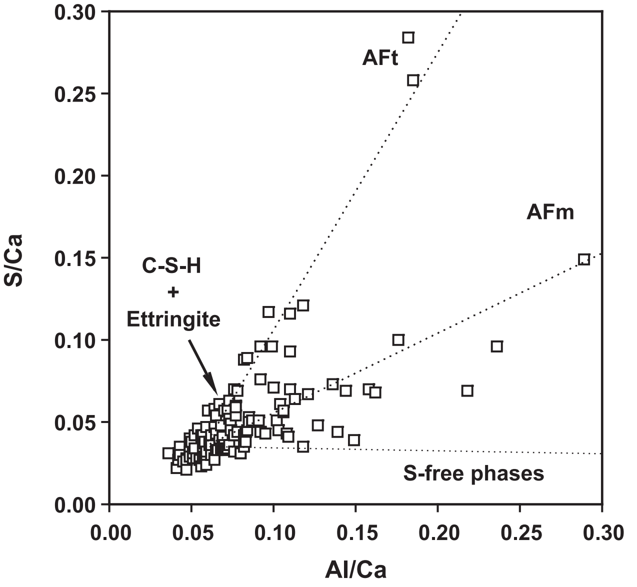

Fig. 10. EDX microanalyses of the outer product in the 95 °C heat-cured Portland cement mortar after 200 days of storage in limewater at ambient temperature.

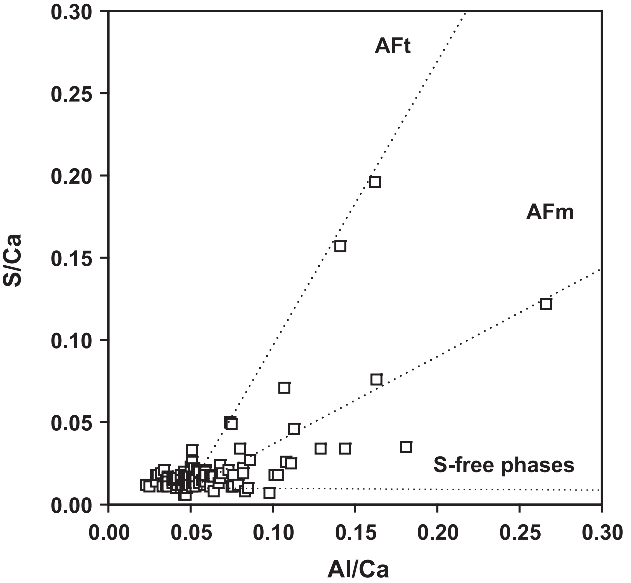

Fig. 11. EDX microanalyses of the outer product in the 95 °C heat-cured Portland cement mortar after 1350 days of storage in limewater at ambient temperature.

S-H at the end of the heat curing, and then recrystallizes elsewhere as larger crystals (i.e., Ostwald ripening).

There is no microscopic evidence of the formation of submicrometer-sized ettringite crystals in the paste in the 95 °C heat-cured Portland cement mortar, as they are likely too small to be resolved in the SEM; however, many larger deposits of ettringite were found in voids and porous regions of the paste, and in the interfacial transition zone (Fig. 12), after several weeks of storage. Around the same time, narrow gaps developed at the paste–aggregate interface and cracks developed in the paste. These gaps and cracks were initially empty, but as expansion proceeded and they widened, ettringite and calcium hydroxide were found filling the gaps and cracks (Fig. 13). The ettringite found in these gaps is likely secondary ettringite and is not believed to generate significant expansive force.

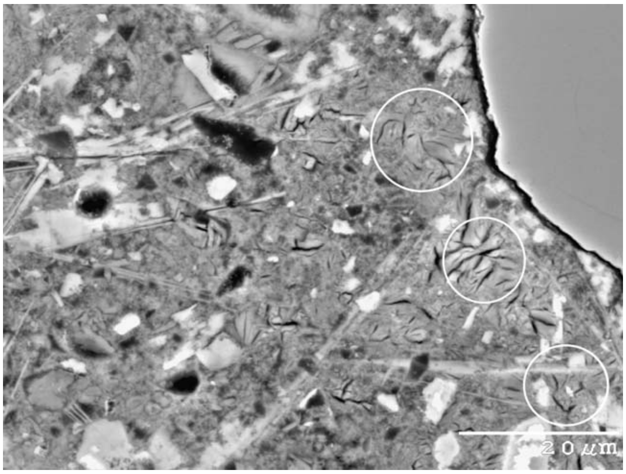

Fig. 12. BEI of 95 °C heat-cured Portland cement mortar after 64 days of storage. Deposits of ettringite (circled) were found in the interfacial transition zone. Narrow empty gaps were observed partially surrounding, and in some instances completely surrounding, aggregate particles. The expansion at this age was 0.04%.

3.4.2. Mortars with silica fume, metakaolin, slag, or fly ash

The microstructural and microanalytical observations of the Portland cement mortar, which expanded following heat curing, presented in the previous section, are largely similar to those reported elsewhere [8,10,11,19]. The following presents microstructural and microanalytical findings of (95 °C) heat-cured mortars containing pozzolans and slag.

With the silica fume and metakaolin mortar, immediately after heat curing at 95 °C the inner C-S-H rims of alite grains were generally darker by BEI and appeared to be less homogeneous than those in the 95 °C Portland cement mortar. They were also slightly smaller in size (~ 3–5 μm thick), which may indicate that there was a lower degree of hydration. It should be noted that with these mixtures a high-range water reducer was used to increase workability, and it is possible that some retardation may have occurred. The inner C-S-H rims of the alite grains in the slag and fly ash mortars more resembled those in the Portland cement mortar in size and appearance.

There were notable differences in the composition of the inner C-S-H with the incorporation of pozzolans and slag. Fig. 14 shows the EDX microanalyses of the inner C-S-H of the blended cement mortars (along with the Portland cement mortar for comparison) directly after heat curing at 95 °C, plotted as S/Ca versus Al/Ca molar ratios. Table 4 gives the mean Mg, Al, Si, S, K, and Ca molar percentages. The percentages of Na, P, Ti, Mn, and Fe were all generally less than 0.3% and are not reported. The Si content was greater when pozzolans and slag were included in the mix, especially with silica fume and Class F fly ash. This is probably due to additional silicon atoms in the structure of the C-S-H

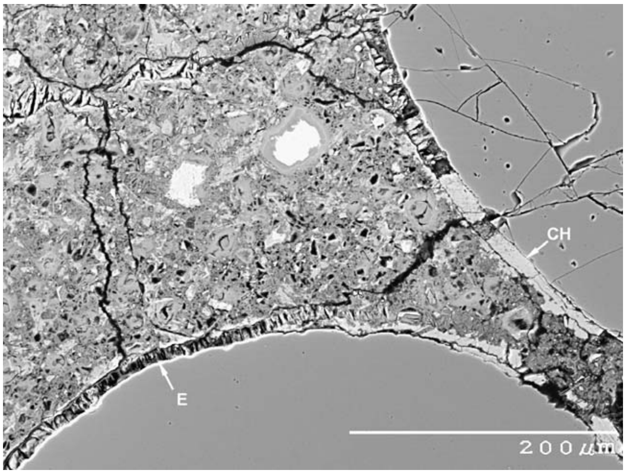

Fig. 13. BEI of 95 °C heat-cured Portland cement mortar after 200 days of storage. Gaps approximately 15 μm thick, filled with both ettringite (E) and calcium hydroxide (CH), were found completely surrounding aggregate particles. The expansion at this age was 2.21%.

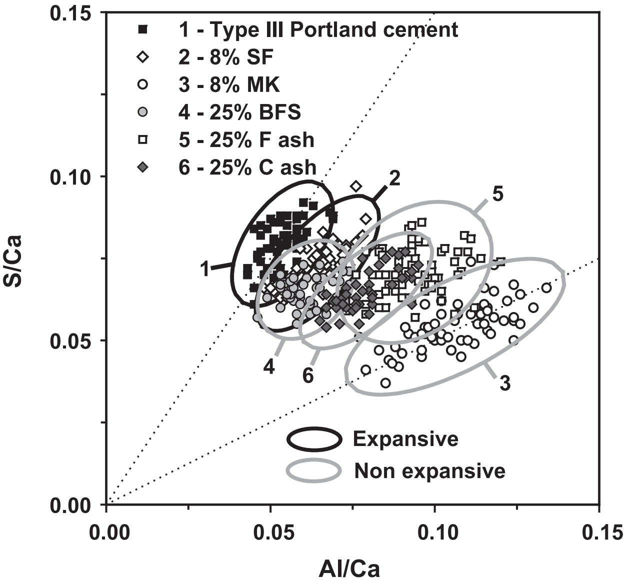

Fig. 14. EDX microanalyses of the inner C-S-H of alite grains in mortars directly after (1 day) heat curing at 95 °C, plotted as the S/Ca versus Al/Ca molar ratios.

derived from the pozzolan or slag. Likewise, with the incorporation of metakaolin or fly ash into the mixture, and to a lesser extent slag, there appeared to be additional aluminum atoms in the C-S-H derived from these materials. Except for the slag specimen, the Ca content of the inner C-S-H was lower in the blended cement mortars, resulting in appreciably lower Ca/Si ratios. The S/Ca molar ratios of the inner C-S-H microanalyses were lower with the incorporation of pozzolans and slag, ranging from 0.054 for the metakaolin specimen to 0.073 for the silica fume specimen. In all of the 95 °C heat-cured specimens, a significant number of microanalyses had S/Ca molar ratios greater than 0.060, which would suggest that a significant amount of sulphate was taken up by the C-S-H during the heat treatment with or without pozzolans and slag in the mixture. More importantly, there is no clear threshold value of S/Ca molar ratio distinguishing expansive mortars from nonexpansive mortars.

Following the heat treatment, the outer product of the silica fume and of the metakaolin heat-cured mortars were typically denser (e.g., less fibrillar in appearance) and had much less visible large-scale porosity than the Portland cement mortar, while the slag and fly ash mortars appeared to have similar porosity to the Portland cement mortar. In all of the blended cement mortars a substantial amount of monosulphate was readily observed by BEI scattered throughout the outer product, especially in the metakaolin mortar. Ettringite was not observed in any of the blended cement mortars following heat curing. EDX analysis of the outer product, in all cases related to monosulphate intermixed on a fine scale with the outer C-S-H; no microanalyses related to ettringite being present directly after heat curing at 95 °C.

After storage in limewater, a significant amount of sulphate was released from the C-S-H with all of the blended cement mortars. Table 4 gives the mean EDX molar percentages after ~ 550 days of storage for the different specimens. In all cases the S/Ca molar ratios decreased significantly during moist storage, at a similar though not identical rate, which would suggest that a comparable amount of sulphate was released from the inner C-S-H with all specimens. The Al/Ca molar ratios also decreased by some extent during storage, with the possible exception of the Class F fly ash specimen, but as with the Portland cement mortar most of the Al remained in the C-S-H after storage.

With the release of sulphate from the C-S-H, a considerable amount of ettringite formed in all of the 95 °C heat-cured blended cement mortars during storage at ambient temperature. However, of these specimens, the silica fume specimen was the only one to expand appreciably during storage. It was also the only one in which were found ettringite-filled gaps at aggregate interfaces and ettringite-filled cracks in the paste (Fig. 15), similar to those found in the 95 °C Portland cement mortar. In the metakaolin, slag,

Table 4
EDX composition of the inner product, which formed at elevated temperature, of alite grains in the Portland cement mortar and blended cement mortars directly after heat curing at 95 °C and after ~ 550 days of continuous storage in limewater at ambient temperature

Mixture	Age (days)	Mg	Al	Si	S	K	Ca	Ca/Si	Al/Ca	S/Ca
Type III only	1	1.01	1.32	11.6	1.95	0.68	24.6	2.13	0.054	0.079
	570	0.97	1.05	13.8	0.40	0.04	25.2	1.83	0.042	0.016
8% Silica fume	1	0.82	1.50	12.8	1.72	0.60	23.5	1.84	0.064	0.073
	530	1.10	1.25	14.1	0.80	0.12	23.6	1.67	0.053	0.034
8% Metakaolin	1	0.90	2.51	12.1	1.28	0.61	23.7	1.95	0.106	0.054
	560	1.17	2.03	13.7	0.48	0.06	23.8	1.74	0.085	0.020
25% Blast-furnace slag	1	0.95	1.51	11.9	1.62	0.44	24.8	2.09	0.061	0.065
	560	1.06	1.37	13.4	0.71	0.02	24.6	1.83	0.056	0.029
25% Class F fly ash	1	1.04	2.11	12.6	1.60	0.85	22.6	1.80	0.094	0.071
	550	0.96	2.14	14.3	0.60	0.13	22.4	1.57	0.095	0.027
25% Class C fly ash	1	1.05	1.86	12.2	1.59	0.52	23.6	1.94	0.079	0.067
	510	0.92	1.65	13.9	0.52	0.05	24.1	1.73	0.069	0.021

The values given are the mean of approximately 30–50 microanalyses.

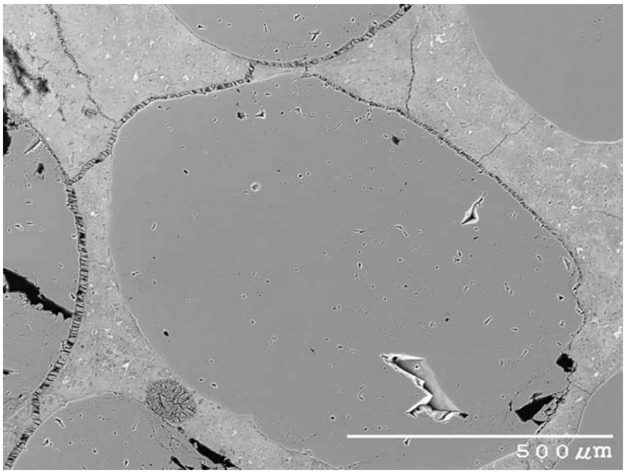

Fig. 15. BEI of 95 °C heat-cured 8% silica fume mortar after 1350 days of storage. The expansion at this age was ∼ 1.06%. Ettringite-filled gaps, cracks, and voids were observed. In general, expansion seemed to be less uniform that in 95 °C-cured Portland cement mortar, and was greater near the surface of the mortar bar.

and fly ash mortars copious amounts of ettringite were found completely filling voids and other porous areas in the cement matrix (Fig. 16), but there were generally no ettringite-filled gaps at the paste–aggregate interface, nor were there ettringite-filled cracks in the paste. Moreover, there was no evidence that the formation of ettringite had caused distress in these mortars.

The reasons for the difference in expansive behaviour between the blended cement mortars are not entirely apparent. Analyses of the outer product in the silica fume mortar were analogous to the heat-cured Portland cement mortar. That is, after 530 days of limewater storage a significant number of the microanalyses related to ettringite being present on a fine scale intermixed with the C-S-H gel in the outer product, indicating that ettringite had formed in the paste (Fig. 17). Furthermore, after 1350 days there was a significant reduction in the sulphate content of the microanalyses of the outer product. Many of the microanalyses still related to monosulphate, but many did not, and none related to ettringite. Together, this would suggest that much of the monosulphate intermixed with the C-S-H gel in the outer product was consumed, as it was in the 95 °C Portland cement mortar, but perhaps at a slower rate, and the ettringite that had formed in the paste on a fine scale had

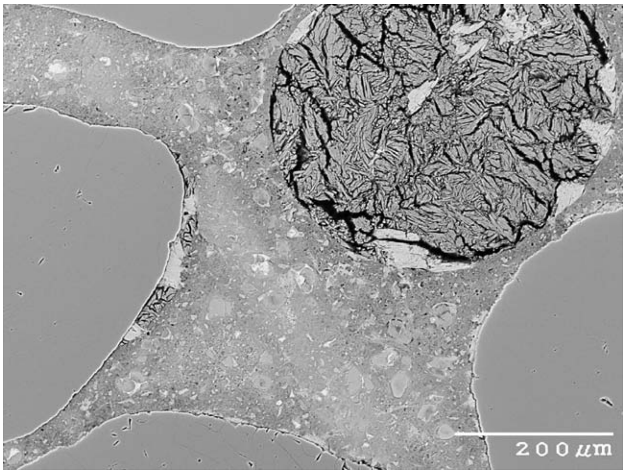

Fig. 16. BEI of 95 °C heat-cured 8% metakaolin mortar after 1350 days of storage. The expansion at this age was ∼ 0.01%. Copious amounts of ettringite were found in large voids and other porous regions in the paste. Note the deposit of ettringite in a void near the surface of an aggregate particle. There is no indication that this has caused distress.

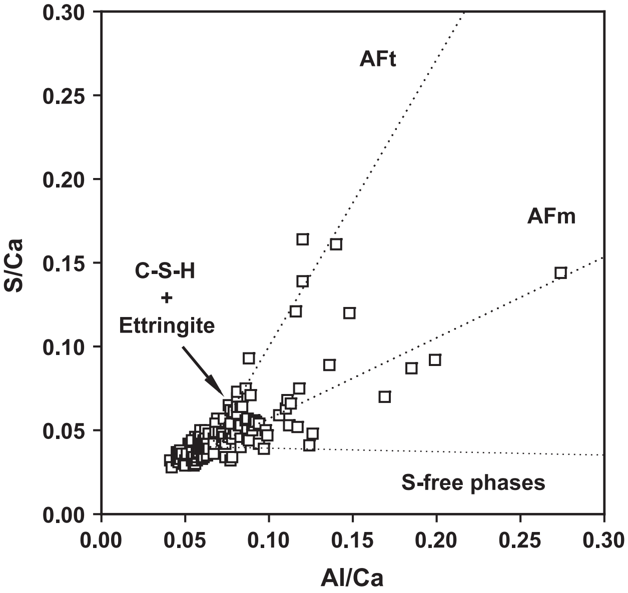

Fig. 17. EDX microanalyses of the outer product in the 95 °C heat-cured 8% silica fume mortar after 530 days of storage in limewater at ambient temperature.

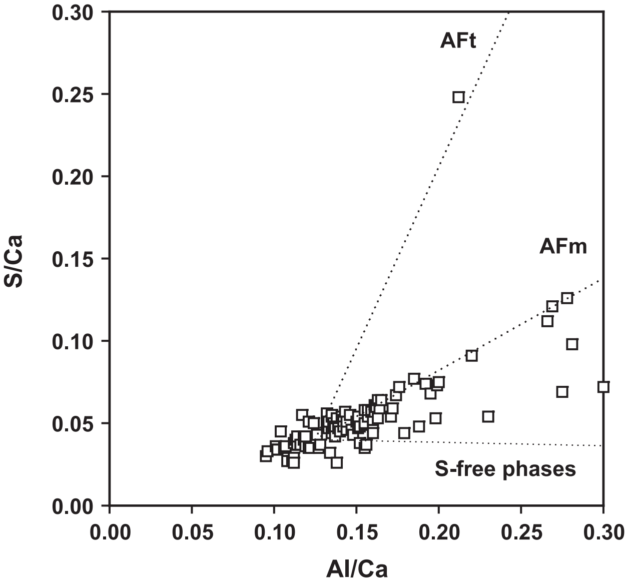

Fig. 18. EDX microanalyses of the outer product in the 95 °C heat-cured 8% metakaolin mortar after 1350 days of storage in limewater at ambient temperature.

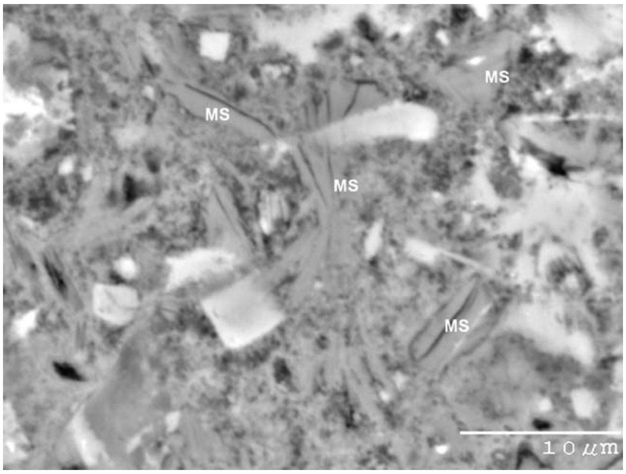

Fig. 19. BEI of the 95 °C heat-cured 8% metakaolin mortar after 1350 days of storage showing large deposits of monosulphate (MS) in the outer product.

later recrystallized in other regions. It should be noted that some larger deposits of monosulphate were still found in the outer product of the silica fume mortar after 1350 days of storage, but the amount present seemed to be less than at earlier ages.

Unlike the heat-cured Portland cement mortar and silica fume mortar, there was no indication of fine intermixing of ettringite with the C-S-H gel in the outer product in the metakaolin, slag, or fly ash mortars after ~ 550 days of storage, though it should be noted that these specimens were not studied by EDX at earlier ages (except directly after the heat treatment). In the metakaolin, slag, and fly ash specimens there was some reduction in the sulphate content of the outer product during storage, but the microanalyses still indicated that there was a considerable amount of intermixing with monosulphate. In particular, even after 1350 days of storage, the microanalyses of the outer product in the metakaolin specimen still had a relatively high sulphate content and they still related to monosulphate intermixed with the outer C-S-H (Fig. 18). Moreover, many large deposits of monosulphate were still found throughout the paste (Fig. 19). This would suggest that the monosulphate was not extensively consumed in the metakaolin mortar, and probably not in the slag and fly ash mortar either, though it should be noted that the latter two specimens were not studied at ages later than ~ 550 days at the time of writing. In the metakaolin, slag, and fly ash specimens the mineral admixture is thought to be a preferential source of Al_2O_3 (i.e., instead of monosulphate) for the formation of ettringite, and ettringite that forms in this manner does not appear to be accompanied by expansion.

4. Discussion

The C-S-H acts as a cache for sulphate; sulphate entering the C-S-H at early age can be released at a later age. The mechanism by which sulphate is taken up by the C-S-H has not been fully explained. It is consistent with an adsorption mechanism, since the sulphate is easily removed from the C-S-H during moist storage.

The composition of the pore fluid plays an important role in the DEF expansion process. The amount of sulphate that is taken up by the C-S-H during the heat cure has been shown to correlate with its concentration in the pore fluid [2], and at later ages, changes in the composition of the pore fluid promote the release of sulphate from the C-S-H.

The initial level of sulphate in the pore fluid is presumably set by the solubility of the alkali sulphates and it changes very little in the first few hours of hydration. In the absence of heating, the sulphate concentration drops to negligible levels by 24 h. However, when curing is done at a sufficiently high temperature the sulphate concentration remains high during the heat cure. This permits a significant amount of sulphate to enter the C-S-H that forms during this time. The capacity of the pore fluid to hold sulphate increases with alkali content, as well as temperature. Cementitious materials that contain a large amount of soluble alkali sulphates, therefore, are likely to yield greater adsorption of sulphate by the C-S-H during the heat curing. In this regard, the alkali content of the cementitious material is probably more important in determining the potential for expansion than the total sulphate content.

Incorporating pozzolans or slag into the mixture as a partial cement replacement can reduce the level of sulphate in the pore fluid during the heat cure. This is partly due to a dilution of the cement sulphates, but is also due to pozzolanic reaction, which can remove K^+ and Na^+ from the pore fluid, and is probably also due to a greater precipitation of sulphate as monosulphate if the replacement material contains sufficient reactive Al_2O_3. A reduction in the sulphate concentration of the pore fluid can result in less adsorption of sulphate by the C-S-H. Notwithstanding, with the blended cement mixtures and curing temperatures investigated in this study, the sulphate concentrations of the pore fluids were all sufficiently high, that a significant amount of sulphate was still taken up by the C-S-H during the heat cure.

Moist storage greatly affects the composition of the pore fluid, especially with the small specimen size used in this study. Leaching of alkalis and hydroxyl from the pore fluid into the host solution lowers the pH and allows more Ca^{2+} to enter the pore fluid. This, as noted by Brown and Shi [22], should result in the removal of sulphate from solution by precipitating ettringite. Ettringite forming from the sulphate remaining in the pore fluid at the end of the heat treatment most likely precipitates innocuously in large voids or in other available spaces and does not contribute to expansion.

Presuming that an equilibrium is established between the sulphate adsorbate and the sulphate in the fluid phase during the heat curing, the removal of sulphate from the pore fluid during moist storage is believed to be equilibrated by desorption of sulphate from the C-S-H by a rate-determining transport process. The rate at which sulphate is desorbed from the C-S-H will be greatest where the sulphate concentration of the pore fluid is very high at the end of the heat cure, and where the sulphate is rapidly removed from the pore fluid during moist storage. It should be appreciated that leaching is not the only mechanism that can promote a desorption of sulphate from the C-S-H. Any mechanism that removes alkali from the pore fluid or lowers its pH, such as alkali–silica reaction (ASR), may have a similar effect.

Famy et al. [23] demonstrated that if the leaching of alkali hydroxides was constrained by storing specimens in KOH solution, the sulphate concentration of the pore fluid tends to remain at a high level and desorption of sulphate from the C-S-H is slowed, retarding the expansion process. A similar effect may occur with a reduction in diffusivity, which may help to explain why, with the silica fume specimen, the onset of expansion was delayed and the rate of expansion was slower. Nevertheless, with the storage conditions used in this study a significant amount of sulphate appears to have been released from the C-S-H during moist storage with all of the blended cement mixtures investigated, and in all cases a considerable amount of ettringite formed.

The mechanism of expansion caused by the formation of ettringite is not fully understood. Expansion is generally believed to result from anisotropic crystal growth; however, there are differing opinions concerning the particular nature of the ettringite formation and its relationship to expansion. Two main hypotheses have been advanced. One theory suggests that expansion results from the nucleation and growth of relatively large ettringite crystals in restricted spaces (e.g., the paste–aggregate interface or preexisting microcracks) [19,24–27]. The other theory suggests that submicrometer-sized crystals of ettringite initially form within the paste from reaction of the monosulphate, which is finely intermixed with the outer C-S-H, with sulphate desorbed from the C-S-H, resulting in a quasi-uniform paste expansion [8,10,28]. The results of this study are inconsistent with the first hypothesis largely because it cannot conceivably explain why the formation of ettringite in the metakaolin, slag, and fly ash specimens did not occur at the paste–aggregate interface or in existing microcracks, resulting in expansion. The results are consistent with the second hypothesis. The microanalytical evidence indicates that in expanding specimens (e.g., the 95 °C Portland cement mortar and the 95 °C 8% silica fume mortar) ettringite forms on a fine scale in the outer product during moist storage consuming the monosulphate that is intermixed with the C-S-H. Thermodynamic considerations of crystal growth in porous media [29] suggest that growth of ettringite in the very small pores (~ 100-nm radius) of the outer product under high supersaturation could results in expansive pressures. This would presume that the necessary species for reaction are present in solution. A solid-state reaction involving sulphate ions and monosulphate crystals, which are a source of Ca^{2+}, $Al(OH)_4^-$, SO_4^{2-}, and OH^- might also produce the chemical and structural transformations that result in the formation of ettringite, and if occurring in very small restricted spaces, could give rise to expansion.

The absence of expansion in specimens incorporating metakaolin, slag, and fly ash is consistent, but not explained by the second hypothesis. In these specimens a considerable amount of ettringite formed during storage, but there was no indication that ettringite formed on a fine scale in the outer product, or that the formation of ettringite consumed the monosulphate intermixed with the outer C-S-H. This fact almost certainly reflects a difference in the way ettringite is formed in the presence of a sufficient amount of a reactive Al_2O_3-bearing mineral admixture. In these specimens, ettringite still forms during moist storage at ambient temperature, but it is deposited in the large voids or other available porous regions of the paste and does not lead to expansion. The reasons for this are not clear. It is hypothesized that the aluminate ionic species derived from the metakaolin, slag, and fly ash have sufficient mobility that they, along with sulphate ions, can migrate through the paste pore structure to voids where ettringite can be deposited without developing expansive pressures. The mineral admixture, therefore, acts as a preferential source of Al_2O_3 for the formation of ettringite averting consumption of the monosulphate.

The above considerations would suggest that the formation of ettringite of itself does not explain expansion. The expansion mechanism is more complex than simple crystal growth. A considerable amount of ettringite can form in a hardened material without any associated expansion. The location where the ettringite forms is more important to the DEF expansion mechanism than the amount of ettringite formed. The replacement of monosulphate by ettringite in the very fine pores of the outer product during moist storage appears to be necessary for the development of expansive pressures. Ettringite forming freely in large voids or other available spaces does not directly contribute to expansion, though it should be appreciated that the filling of air voids with ettringite may have other durability concerns.

Further study is required to fully understand the role of monosulphate in the DEF expansion process and how it changes in the presence of other sources of Al_2O_3.

5. Conclusions

1. Incorporation of pozzolans or slag into the mixture modified the inner product of the alite phase, but it did not differ significantly in composition from that where Portland cement was the only binder. The Ca/Si ratio of the inner C-S-H was reduced. Some Si^{4+} and Al^{3+} from the pozzolan or slag entered the C-S-H giving somewhat different molar ratios. Significantly more Al^{3+} entered the C-S-H gel with the use of metakaolin, slag, and fly ash.

2. The sulphate and aluminate were partitioned differently amongst the pore fluid and the solid phases with the use of pozzolans and slag. Less sulphate was typically present in the pore fluid and in the C-S-H at the end of the heat cure, and with the possible exception of the silica fume specimen, more sulphate appeared to be accommodated in the monosulphate phase. A hydrogarnet-type phase formed in greater amounts with use of fly ash, and perhaps also metakaolin and slag, accommodating some of the aluminate. Some aluminate was also contained in a hydrotalcite-type phase with incorporation of slag. Neither the hydrogarnet-type or hydrotalcite-type phase appears to react with sulphate. No ettringite was present at the end of the 95 °C heat cure.
3. The microstructure was modified with the addition of pozzolans or slag. The outer C-S-H appeared less fibrillar and the cement matrix was less porous at earlier ages with use of silica fume or metakaolin. The effect of this was a reduced rate of leaching of the alkali hydroxide from the pore fluid, which with the silica fume specimen appeared to slow the expansion process, but did not prevent expansion.
4. A significant amount of sulphate was taken up by the C-S-H during heat curing, both with mixtures containing only Portland cement as the binder and with partial amounts of silica fume, metakaolin, blast-furnace slag, and fly ash. The C-S-H acts like a cache and this sulphate was later released when the specimens were exposed to moisture at ambient temperature. In all specimens, a considerable amount of ettringite formed in the hardened material, but only with the Portland cement mortar and the silica fume mortar was the formation of ettringite accompanied by expansion.
5. The formation of ettringite is not expansive, per se. Significant amounts of ettringite may form without expansion. The microanalytical evidence suggests that monosulphate was finely intermixed with the C-S-H gel in the outer product at the end of the heat treatment. In specimens that expanded during moist storage at ambient temperature this monosulphate was replaced by ettringite, which initially formed also on a fine scale intermixed with the C-S-H gel in the outer product. With the incorporation of a sufficient amount of an Al_2O_3-bearing mineral admixture this did not appear to occur. A large amount of ettringite still formed during moist storage, but it was not accompanied by expansion.

Acknowledgements

The authors gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada and Lafarge North America for their support of this project.

References

[1] T. Ramlochan, P. Zacarias, M.D.A. Thomas, R.D. Hooton, The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature: Part I. Expansive behaviour, Cem. Concr. Res. 33 (6) (2003) 807–814.

[2] T. Ramlochan, The effect of pozzolans and slag on the expansion of mortars and concrete cured at elevated temperature, PhD thesis, University of Toronto, 2003.

[3] G.L. Kalousek, M. Adams, Hydration products formed in cement pastes at 25 to 175 °C, J. Am. Conc. Inst. (Proc.) 48 (1) (1951) 77–90.

[4] P.W. Brown, J.V. Bothe, The stability of ettringite, Adv. Cem. Res. 5 (18) (1993) 47–63.

[5] W. Wieker, R. Herr, On some problems of the chemistry of Portland cement, Z. Chem. 29 (9) (1989) 321–327.

[6] S. Ong, Studies on effects of steam curing and alkali hydroxide additions on pore solution chemistry, microstructure, and alkali silica reaction, PhD thesis, Purdue University, 1993.

[7] F.P. Glasser, D. Damidot, M. Atkins, Phase development in cement in relation to the secondary ettringite problem, Adv. Cem. Res. 7 (26) (1995) 57–68.

[8] C. Famy, Expansion of heat-cured mortars, PhD thesis, Imperial College of Science, University of London, 1999.

[9] H.F.W. Taylor, C. Famy, K.L. Scrivener, Delayed ettringite formation, Cem. Concr. Res. 31 (5) (2001) 683–693.

[10] K.L. Scrivener, H.F.W. Taylor, Delayed ettringite formation: a microstructural and microanalytical study, Adv. Cem. Res. 5 (20) (1993) 139–146.

[11] M.C. Lewis, Heat curing and delayed ettringite formation in concretes, PhD thesis, Imperial College of Science, University of London, 1996.

[12] R. Yang, C.D. Lawrence, J.H. Sharp, Delayed ettringite formation in 4-year old cement pastes, Cem. Concr. Res. 26 (11) (1996) 1649–1659.

[13] I.G. Richardson, G.W. Groves, Incorporation of minor and trace elements into calcium silicate hydrate (C-S-H) gel in hardened cement pastes, Cem. Concr. Res. 23 (1) (1993) 131–138.

[14] A.M. Harrison, N.B. Winter, H.F.W. Taylor, An examination of some pure and composite Portland cement pastes using scanning electron microscopy with X-ray analytical capability, 8th ICCC Brazil, vol. 4, Alba Grafica e Editoria, Rio de Janeiro, Brazil, 1986, pp. 170–175.

[15] D. Bonen, S. Diamond, Interpretation of compositional patterns found by quantitative energy dispersive X-ray analysis for cement paste constituents, J. Am. Ceram. Soc. 77 (7) (1994) 1875–1882.

[16] I.G. Richardson, The nature of C-S-H in hardened cements, Cem. Concr. Res. 29 (8) (1999) 1131–1147.

[17] I. Odler, Interaction between gypsum and the C-S-H phase formed in C_3S hydration, 7th ICCC, Paris 1980, vol. 4, Editions Septima, Paris, France, 1981, pp. 493–495.

[18] I. Odler, Y. Chen, Effect of cement composition on the expansion of heat-cured cement pastes, Cem. Concr. Res. 25 (4) (1995) 853–862.

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

[20] P. Longuet, L. Burglen, A. Zelwer, The liquid phase of hydrated cement, Rev. Mater. Constr. 676 (1973) 35.

[21] R.S. Barneyback, S. Diamond, Expression and analysis of pore fluids from hardened cement pastes and mortars, Cem. Concr. Res. 11 (2) (1981) 279–285.

[22] P.W. Brown, D. Shi, A model for the variation in solution chemistry during tricalcium silicate hydration, Adv. Cem. Res. 4 (1) (1992) 17–27.

[23] C. Famy, K.L. Scrivener, A. Atkinson, A.R. Brough, Influence of the storage conditions on the dimensional changes of heat-cured mortars, Cem. Concr. Res. 31 (5) (2001) 795–803.

[24] D. Heinz, U. Ludwig, Mechanism of secondary ettringite formation

in mortars and concretes subjected to heat treatment, in: J.M. Scanlon (Ed.), Concrete Durability, Katherine and Bryant Mather Int. Conf., ACI SP-100, vol. 2. American Concrete Institute, Detroit, 1987, pp. 2059–2071.

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

[26] S. Diamond, Delayed ettringite formation—processes and problems, Cem. Conc. Compos. 18 (3).

[27] Y. Fu, J.J. Beaudoin, Microcracking as a precursor to delayed ettringite formation in cement systems, Cem. Concr. Res. 26 (10) (1996) 1493–1498.

[28] V. Johansen, J. Thaulow, J. Skalny, Simultaneous presence of alkali–silica gel and ettringite in concrete, Adv. Cem. Res. 5 (17) (1993) 23–29.

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