Cement & Concrete Composites 25 (2003) 861–865

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

Evolution of ettringite in presence of carbonate, and silicate ions

I. Pajares [a], S. Martínez-Ramírez [b,*], M.T. Blanco-Varela [a]

[a] Instituto Eduardo Torroja de Ciencias de la Construcción (CSIC), C/Serrano Galvache s/n, 28033 Madrid, Spain
[b] Instituto de Estructura de la Materia (CSIC), C/Serrano 121, 28006 Madrid, Spain

Abstract

The main objective of this work was to study the evolution of ettringite when in contact with a solution containing carbonate and silicate ions.

Ettringite was synthesised and put in contact with three types of saturated solutions: (a) $CaCO_3$ and silica gel saturated solution; (b) $MgCO_3$ and silica gel saturated solution and (c) C–S–H gel plus portlandite and $CaCO_3$ saturated solution. The temperature of the experiment was 4 ± 2 °C. At different ages the samples were studied by: FTIR, XRD, NMR, and SEM/EDX.

Ettringite evolves with time, reacting with carbonates and silicates and decomposing to poorly crystallised products when it is in contact with solutions (a) and (b). Ettringite decomposition rate is much higher when it is in contact with saturated magnesium carbonate solution (b) than when in contact with the solution (a). After 90 days of exposure in solution (b) ettringite decomposition starts, followed by reorganization of the atoms giving place to a semi-stable poorly crystallised compound. However 130 days are necessary for ettringite decomposition in solution (a). Ettringite in contact with solution (c) evolves more slowly and it almost remains unchanged after 380 days of treatment. $Ca(OH)_2$ formed in the C_3S and C_2S hydration retards ettringite decomposition.

Keywords: Ettringite; Thaumasite; Solid solution

1. Introduction

Ettringite evolution and its possible transformation into thaumasite in mortars and concretes of Portland cement is a current subject of research, because it presents some aspects scarcely defined in the available bibliography.

Ettringite is a complex calcium salt, for which most of the authors acknowledge the stochiometrical formula: $(Ca_6[Al(OH)_6]_2(SO_4)_3 26H_2O)$. This mineral is formed in the early stages of Portland cement hydration by the reaction of the aluminate phase with water and calcium sulphate.

Reaction of cement minerals with sulphate and carbonate ions can lead to thaumasite formation $(Ca_6[Si(OH)_6]_2(CO_3)_2(SO_4)_2 24H_2O)$. Some authors sustain that ettringite comes from the transformation is a precursor in the formation of thaumasite. Kollman and Strübel [1], for instance, report that if the silicate in the CSH gel dissolves—or the Si^{4+} is incorporated or combined—in the presence of carbonate and at temperatures from 1 to 5 °C, ettringite "turns into" thaumasite almost quantitatively after 40 days, in a process accompanied by expansion. Other authors [2] claim that ettringite exerts a catalytic effect on thaumasite formation.

The very similar structure of both phases thaumasite and ettringite, seems to support the hypothesis that thaumasite comes from the transformation of ettringite [3–5]. The most generalized criterion has until now been that formation of thaumasite in mortars and concretes occurs as a consequence of the evolution of ettringite when it incorporates Si^{4+} (in octahedral coordination) into its structure, substituting the Al^{3+} ions. The presence of CO_3^{2-} is, indeed, also necessary. Nonetheless, this mechanism for thaumasite formation assumes that the two compounds exist in a continuous solid solution.

The crystal structure of thaumasite [6] and ettringite [7] are closely related, and substitution of Al by Si and partial replacement of the interstitial SO_4^{2-} with CO_3^{2-} ions in ettringite may lead to the formation of solid solutions between the two minerals [8–10]. Carpenter [11] reported the occurrence of oriented overgrowths of thaumasite on ettringite. He reported that both thaumasite and ettringite had "anomalous refractive indices"

---

* Corresponding author. Tel.: +34-91-5616800; fax: +34-91-5645557.
E-mail address: pesm104@ietcc.csic.es (S. Martínez-Ramírez).

0958-9465/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0958-9465(03)00113-6

and suggested that some form of solid solution may exist. Edge and Taylor [12] concluded that the close similarity between the two structures supported the suggestion that solid solutions could exist, while the fact that the space groups are different and the *c*-axis of ettringite is doubled hints that there might be some sort of discontinuity or gap in any solid solution. Bensted and Varma [13] consider that the structures of thaumasite and ettringite are too dissimilar for the existence of any substantial solid solution. Nevertheless, on occasions, it has been proven in real concrete that the formation of thaumasite in the presence of ettringite does not indicate a continuous solid solution series but a mixture of these two hydrates [14].

Barnett et al. [15–18] have recently shown the existence of a gap in the solid solution of the two substances, and they have established limits for the substitution of Si for Al in the structure of ettringite and for aluminium for silica in thaumasite structure. This would appear to rule out the possibility of topochemical substitution of thaumasite for ettringite as a possible mechanism in the formation of the former product in mortars and concretes.

There are experimental evidences in the literature that support the existence of thaumasite–ettringite solid solutions, however the evolution and crystal changes in relation with the amount of Si substituting Al in ettringite are not known.

The main objective of this work is to study the ettringite evolution in different solutions containing carbonate and silicate ions from several sources: calcite, magnesium carbonate, silica gel, CSH gel.

2. Experimental

Lime and $Al_2(SO_4)_3 \cdot 18H_2O$, pure grade were mixed in a sucrose solution in order to synthesise ettringite according to the Struble procedure [19]. The precipitate was identified as pure ettringite by X-ray diffraction.

The ettringite was put in contact with three types of saturated solutions: (i) $CaCO_3$ and silica gel saturated solution; (ii) $MgCO_3$ and silica gel saturated solution and (iii) C–S–H gel plus portlandite and $CaCO_3$ saturated solution. In order to maintain the saturated solutions and to avoid direct contact of ettringite, with the solutions, calcite, magnesium carbonates, silica gel etc., were put in permeable bags hanging in the water. The temperature of the experiment was 4 ± 2 °C. Everyday the solutions were agitated for 5 min. At 28, 56, 70, 90, 130, 170, 210, 250, 290, 340 and 380 days the samples were removed by vacuum filtration and dried in a desiccator. Mineralogical composition of the solid phase was studied by FTIR, XRD. Certain selected samples were also examined using Raman spectroscopy, NMR, ^{29}Si MASNMR and ^{27}Al MAS NMR techniques.

3. Results and discussion

Figs. 1–3 show the FTIR spectra where the evolution and the main changes in the ettringite structure in the three saturated solutions can be seen. Figs. 4–6 illustrate X-ray diffraction of the same samples. Pure ettringite as reference is used in the studied cases.

3.1. Ettringite + $CaCO_3$ + silica gel

Ettringite evolution over the exposure time is shown in Fig. 1. After 28 days of contact a shoulder at 1014 cm^{-1} appears. This band can be due to C–S–H gel formed when silica gel reacts with calcium of ettringite. Different bands at 1490, 1448 and 1422 cm^{-1} show the presence of CO_3^{2-} in the sample. The FT-Raman spectra

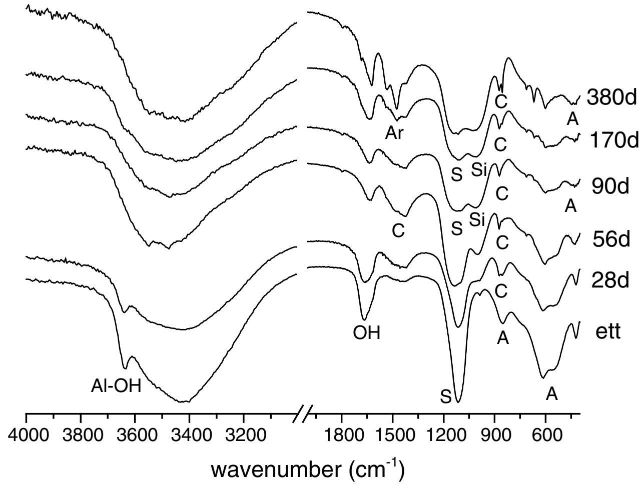

Fig. 1. FTIR of the ettringite in contact with $CaCO_3$ and silica gel solution at different ages. C—CO_3^{2-}; S—SO_4^{2-}; Si—SiO_4^{2-}; A—Al; Ar—Aragonite.

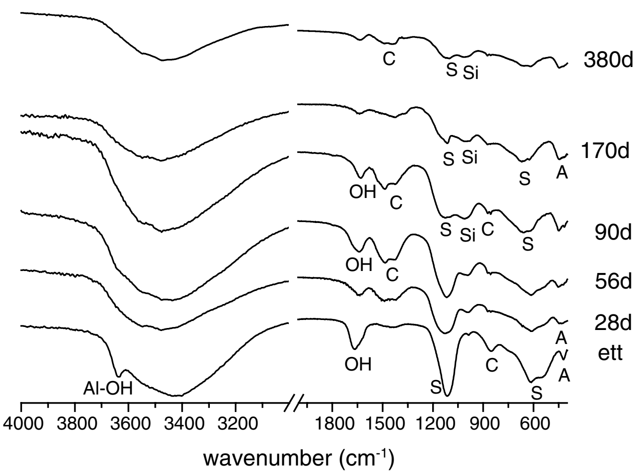

Fig. 2. FTIR of the ettringite in contact with $MgCO_3$ and silica gel solution at different ages. C—CO_3^{2-}; S—SO_4^{2-}; Si—SiO_4^{2-}; A—Al.

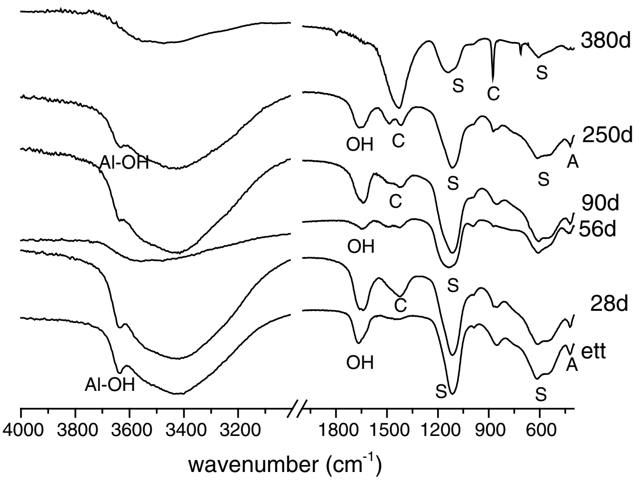

Fig. 3. FTIR of the ettringite in contact with $CaCO_3$ and $C_3S + C_2S$ solution at different ages. C—CO_3^{2-}; S—SO_4^{2-}; Si—SiO_4^{2-}; A—Al.

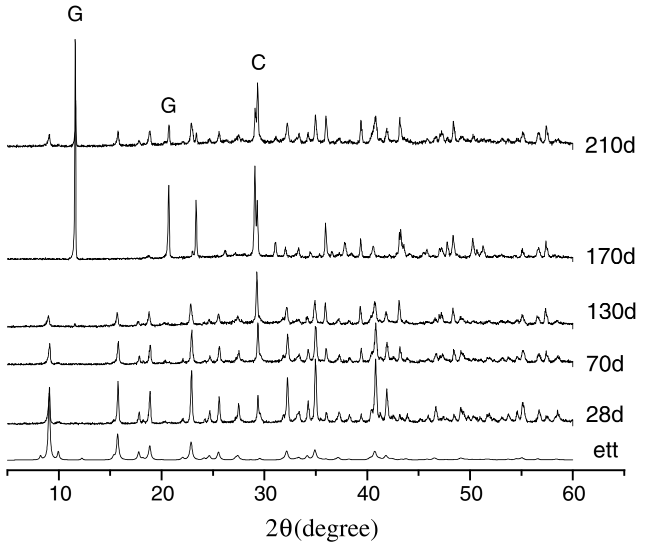

Fig. 4. XRD of the ettringite in contact with $CaCO_3$ and silica gel solution at different ages. G—gypsum; C—calcite.

confirm the presence of calcite and other carbonates possibly bonded to the ettringite structure. Calcite presence was confirmed by X-ray diffraction (Fig. 4).

Sharp bands at 3645 and 856 cm^{-1} respectively due to the free O–H stretching and Al–O–H bending vibrations disappear after 70 days of treatment. This can suggest a change in the ettringite structure. However no X-ray diffraction modifications have been observed. The carbonate bands were similar to the bands observed in the 28-day sample. The shoulder appearing in the FTIR spectrum of 28-days sample due to the Si–O stretching vibrations in the CSH gel evolved into a band at 1000 cm^{-1}. In order to clarify this discrepancy the sample was studied by SEM/EDAX, EDAX analysis which revealed a decrease in S and Al increase, indicating that ettringite has been partially decomposed.

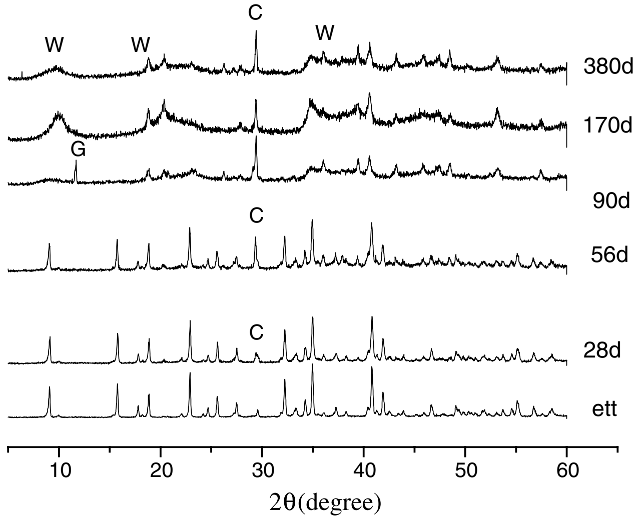

Fig. 5. XRD of the ettringite in contact with $MgCO_3$ and silica gel solution at different ages. W—woodfordite; G—gypsum; C—calcite.

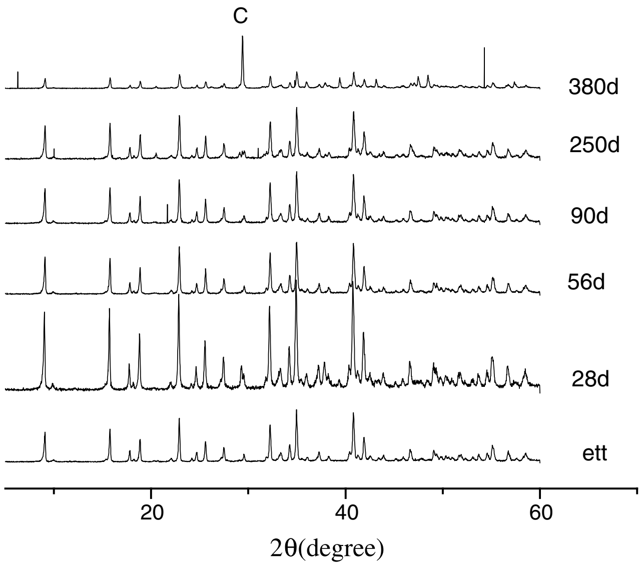

Fig. 6. XRD of the ettringite in contact with $CaCO_3$ and $C_3S + C_2S$ solution at different ages. C—calcite.

The sample filtered after 70 days was analysed by ^{29}Si MASNMR and ^{27}Al NMR and FTIR spectroscopy. Two bands, at −59 and −85 ppm, corresponding to calcium silicate hydrates (CSH gel) [20], were recorded in the broad profile of the ^{29}Si MASNMR spectrum, which were assigned to Q^0 and Q^2, respectively. Two bands were also recorded in the ^{27}Al NMR spectrum: one at 13.03 ppm, corresponding to the Al in the octahedral co-ordination of ettringite, and the other at 60.37 ppm, due to the Al in tetrahedral coordination included in the CSH gel silicate chain [20].

These changes reveal the progressive damage in the crystal structure of ettringite and confirm the FTIR findings, which indicated the CSH formation and the partial ettringite decomposition 70 days into the trial.

Gypsum shows up in the sample after 130 days and after 170 days gypsum presence is even higher than ettringite. In the same way CO_3^{2-} bands increase and aragonite bands appear. These results can be observed by both FTIR and XRD.

Then at 210 days ettringite bands and peaks disappear from XRD and FTIR patterns indicating full decomposition of ettringite. At higher ages FTIR of the sample shows two bands appearing at 800 and 472 cm^{-1}. They can be attributed to AlO_4 groups.

In keeping with these results, the dissolution of ettringite in water produces calcium ions that react with the silicate and carbonate ions in the solution, forming a CSH gel containing Al in its structure and calcium carbonates (calcite and aragonite). These reactions prompt further ettringite dissolution while lowering the pH of the solution and thereby contributing to destabilisation of the compound. According to Myneni et al. [21], ettringite dissolves congruently at about pH 10.7; below this pH ettringite can exist only in association with gypsum and gibbsite. In the present experiment, the pH of the solution decreased throughout the trial, reaching a value of 8.3 after 11 months. Neither ettringite nor thaumasite are stable at that pH.

3.2. Ettringite + $MgCO_3$ + silica gel

At 28 days FTIR of the sample shows similar modifications compared with the ettringite in contact with $CaCO_3$ and silica gel. FTIR spectrum showed several changes: both the O–H stretching band at 3631 cm^{-1} and the O–H bending band at 852 cm^{-1} disappeared; two new bands appeared: one at 992 cm^{-1} corresponding to Si–O stretching vibrations in the CSH gel and the other at 1420–1490 cm^{-1} assigned to C–O vibration of the carbonate ion; the band at 1114 cm^{-1} due to S–O vibrations shifted to 1130 cm^{-1} ; finally, the water band at 1666 cm^{-1} shifted to 1639 cm^{-1}. XRD of this sample shows peaks from ettringite and very small reflections due to calcite.

After 56 days of exposure small bands at 1013 cm^{-1} and 994 overlapping can be seen. Both of them could be assigned to SiO_4 group vibrations. XRD of this sample shows peaks from ettringite, calcite and aragonite.

Ninety days into the trial the ettringite had decomposed completely and gypsum, bayerite, calcite and aragonite were identified with XRD and FTIR techniques. The broad peaks in the XRD pattern were indicative as well of a very poorly crystallised product in the sample.

This is most clear at 170 days. No gypsum peaks were identified in the XRD pattern for the 170-day sample, while the forementioned broad peaks indicative of a poorly crystallised product increased.

These result can suggest that ettringite decomposition starts after 90 days of exposure, followed by reorganization of the atoms giving place to a semi-stable poorly crystallised compound with an structure like woodfordite ($Ca_6Al_2(SO_4,SiO_4,CO_3)_3(OH)_{12}26H_2O$) [22] according to X-ray diffraction pattern of the sample. Not much information can be drawn from bibliography about this compound.

From FTIR it is clear that there is the presence of a broad band at 1005–985 cm^{-1} as well a shoulder at 1373 cm^{-1}. The broad band can be attributed to silicates and the shoulder to CO_3^{2-} groups introduced into the ettringite structure similar to the ones in thaumasite.

At 380 days of exposure, FTIR and XRD of the sample are similar to the ones at 170 days of exposure.

Under these conditions calcium ions from the dissolution of ettringite in water react with silicate (as in the preceding case) and carbonates ions (from $MgCO_3$) to produce a CSH gel and calcium carbonate (calcite plus aragonite), respectively. Ettringite decomposes more quickly under these conditions than in the preceding experiment due to the higher solubility of magnesite than calcite. The pH decreased throughout the trial in this case also, dropping to a value of 8.3 at 11 months, although no thaumasite formation was observed.

3.3. Ettringite + $CaCO_3$ + C_2S + C_3S

Until 56 days of exposure no significant changes have been observed by either FTIR or XRD (Figs. 3 and 6). At this age bands at 3630, 856 and 567 cm^{-1} associated with Al–OH disappear. A new band at 1490 cm^{-1} from CO_3^{2-} appears. The SO_4^{2-} band is shifted from 1117 to 1136 cm^{-1} indicating a little change in the ettringite structure. These modifications are similar to the ones produce in the sample in contact with $CaCO_3$ and silica gel (solution (i)).

After 90 days of exposure the FTIR spectrum is similar to the ettringite reference. According to Zhou [23] partial regeneration of ettringite may occur in certain conditions, high humidity and low carbonate content. In this solution C_2S and C_3S reacts with water giving place to C–S–H gel and portlandite. Calcite dissolution in water decreases in $Ca(OH)_2$ presence according to Le Chatelier Law. Ettringite in contact with solution (iii) has the conditions for ettringite regeneration.

The samples filtered after 130 and 250 days were analysed by ^{29}Si NMR spectroscopy. Two bands at −60 and −85 ppm corresponding to Si tetrahedrical coordination characteristic of C–S–H gel have been observed. This CSH gel became from calcium silicate hydration rather than the ettringite decomposition.

From 340 and 380 days an increase in calcite is observed in the sample, however no gypsum is detected, suggesting no ettringite decomposition. The pH of the solution is 11.3. At this pH level thaumasite can be formed.

4. Conclusions

Ettringite evolution in the studied solutions proceeds under different way. In the presence of $CaCO_3$ and silica gel, ettringite decomposition starts at 130 days. When $MgCO_3$ is present instead of $CaCO_3$, ettringite decomposition starts at 90 days. Additionally in this solution a new semi-stable amorphous compound has been formed.

For the samples exposed in $CaCO_3$ and $C_2S + C_3S$ solution it is important to remark that $Ca(OH)_2$ formation retards ettringite decomposition. Since 340 days are necessary until ettringite decomposition starting.

Acknowledgements

The PGC programme Project PB98-0518 supported this study. S. Martínez-Ramírez wish to thank to DGES (MEC) for the "Contrato de Incorporación de Doctores" given to her. I.Pajares wish to thank to MCYT for the FPI grant.

References

[1] Kollman H, Strübel G. Experimental studies on the question solid solution formation between ettringite and thaumasite. Fortschr Mineral 1978;56(1):65–6.

[2] Lachaud R. Thaumasite and ettringite in building materials. ITBTP Ann 1979;370:3.

[3] Bensted J. Thaumasite—background and nature in deterioration of cements, mortars and concretes. Cem Concr Compos 1999; 21:117–21.

[4] Baronio G, Berra M. Concrete deterioration with the formation of thaumasite. Anal Causes, II Cemento 1984;83(3):169–84.

[5] Crammond NJ. Thaumasite in failed cement mortars and renders from exposed brickwork. Cem Concr Res 1985;15:1039–50.

[6] Edge RA, Taylor HFW. Crystal structure of thaumasite, $[Ca_3Si(OH)_6 12H_2O](SO_4)(CO_3)$. Acta Crystallogr B 1971;27: 594–601.

[7] Moore AE, Taylor HFW. Crystal structure of ettringite. Acta Crystallogr B 1970;26:386–93.

[8] Lukas W. Substitution of Si in the lattice of ettringite. Cem Concr Res 1976;6:225–34.

[9] Barnett SJ, Adam CD, Jackson ARW. Solid solutions between ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}26H_2O$, and thaumasite Ca_3SiSO_4-$CO_3(OH)_6 12H_2O$. J Mater Sci 2000;35:4109–14.

[10] Barnett SJ, Adam CD, Jackson ARW. An XRPD profile fitting investigation of the solid solution between ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}26H_2O$, and carbonate ettringite, $Ca_6Al_2(CO_3)_3(OH)_{12}26H2O$. Cem Concr Res 2001;31:13–7.

[11] Carpenter AB. Oriented overgrowths of thaumasite on ettringite. Am Miner 1963;48:1394–6.

[12] Edge RA, Taylor HFW. Crystal structure of thaumasite Sec. 27 Acta Crystallogr 1971;(Pt. 3):594–601;
Nature 1969;224(5217):363–4.

[13] Bensted J, Varma SP. Studies of thaumasite—Part II. Silic Ind 1974;39(1):11–9.

[14] Kollman H, Strubel G, Trost F. Mineralsynthetische Untersuchungen zu Treibursachen durch Ca–Al–Hydrat und Ca–Si–Carbonat–Hydrat. Tonindustrie-Zetung und keramische Rundschau 1977;101(3):3–70.

[15] Barnett SJ, Macphee DE, Lachowski EE, Crammond NJ. XRD, EDX and IR analysis of solid solutions between thaumasite and ettringite. Cem Concr Res 2002;32:1–12.

[16] Barnett SJ, Macphee DE, Crammond NJ. Extent of immiscibility in the ettringite–thaumasite system. In: Proceedings of the First International Conference on Thaumasite in Cementitious Materials, Garston, UK. Paper 1, 19–21 June 2002.

[17] Lachowski EE, Barnett SJ, Macphee DE, Cramond NJ, XRD, SAED and EDX analysis of thaumasite/ettringite solid solutions. Kurdowski Symposium, Science of Cement and Concrete, Krakow; 2001. p. 199–206.

[18] Barnettt SJ, Adam CD, Jackson ARW, Hywel-Evans PD. Identification and characterization of thaumasite by XRPD techniques. Cem Concr Compos 1999;21:123–8.

[19] Struble LJ. Synthesis and characterization of ettringite and related phases. In: 8th International Congress on the Chemistry of Cement. 1986;VI:582–8.

[20] Fernández-Jiménez A, Puertas F, Sobrados I, Sanz J. Structure of calcium silicate hydrate formed in alkaline activated slag. Influence of the type of alkaline activator. J Am Ceram Soc, in press.

[21] Myneni SCB, Traina SJ, Logan TJ. Ettringite solubility in geochemistry of $Ca(OH)_2$–$Al_2(SO_4)_3$–H_2O system at I atm pressure and 298 K. Chem Geol 1998;148:1–19.

[22] Murdoch J, Chalmers RA. Ettringite (woodfordite) from crestmore. Calif Am Mineral 1960;45:1275–8.

[23] Zhou Q, Glasser FP. Kinetics and mechanism of the carbonation of ettringite. Adv Cem Res 2000;12(3):131–6.