FORMATION AND STABILITY OF C–S–H(I) IN Ca(OH)₂/CaO–THERMAL SILICA DENSIFIED–H₂O SYSTEM

KESTUTIS BALTAKYS, RAOUL JAUBERTHIE*, VITA KASPERAVICIUTE

Department of Silicate Technology, Kaunas University of Technology, Radvilenu 19, LT – 50270 Kaunas, Lithuania *Department of Civil Engineering, INSA, 20 Av. des Buttes de Coësmes, CS 14315, 35043 Rennes, France

E-mail: kestutis.baltakys@ktu.lt

Submitted September 25, 2008; accepted January 30, 2009

Keywords: Calcium silicate hydrates; C-S-H(I); Xonotlite; X-Ray Diffraction

The stability and crystals morphology of C–S–H(I) in the CaO/Ca(OH)₂–TSD–H₂O systems and a sequence of intermediary compound formation has been examined. Two series of samples, each being made with different forms of CaO and SiO₂, were used in the experimental tests. The molar ratio of primary mixtures was CaO/SiO₂ = 1.0. Hydrothermal synthesis has been carried out under the saturated steam pressure at temperatures of 90, 110, 130, 150 and 175°C; the duration of isothermal curing was 2, 8, 24 or 72 hours. It was determined that thermal silica densified has negative influence on the formation of calcium silicate hydrates. Ca²⁺ containing components (Ca(OH)₂, CaO) change the composition of intermediate and final products of the synthesis. In the mixtures with Ca(OH)₂, intermediary and final compound is C–S–H(I) in different crystalline degree. Meanwhile, in the mixtures with CaO, the main intermediary compound is C–S–H(I) and the main product is xonotlite. It was estimated that the increment of temperature significantly influences the stability, morphology and crystalline degree of C–S–H(I).

INTRODUCTION

C–S–H is the primary strength-forming phase in Portland cement paste and significantly influences it's mechanical and transport properties. C–S–H has a wide compositional range, with molar CaO/SiO₂ (C/S) ratios between 0.6 and more than 2. The C/S ratios of C–S–H precipitated from aqueous solution depend on the C/S ratios of starting materials, with higher C/S ratios in the starting materials usually resulting in higher C/S ratios in the final products. C/S ratios less than 0.6 usually occur when excess silica is present [1-7].

There are many proposed structural models for C-S-H, all of which involve some kind of layer structure as revealed by many instrumental analysis methods data. They differ in the details of the individual layers, how the layers are connected, and what is in the interlayer [8-15].

T. Mitsuda et al. [16] determined that C–S–H(I) was always formed as an initial product of crystalline phase. These results for crystalline phases formed after C–S–H agreed with those reported by many workers. It should be underlined that C–S–H(I) phase is metastable and presents a tendency to crystallization [17-18]. It transforms to tobermorite but this processis very slow, probably due to difficulties in nucleation. The elevated temperatures accelerate the transformation and high pressure seems to be even more efficient. In the majority of cases the product of transformation presents a mixture

of C–S–H(I) and tobermorite [19]. Meanwhile, in the low base (C/S \sim 0.6) mixtures the initial C–S–H gel transforms to Z-phase and then finally recrystallizes to gyrolite [20-25].

This paper reviews recent results from our laboratory concerning with the possibility to use more by-products (especially the compounds which have silicon and calcium components) as secondary raw materials in the synthesis of calcium silicate hydrates.

The aim of this paper was to examine the stability and crystals morphology of C–S–H(I) in the CaO/ /Ca(OH)₂ and thermal silica densified mixtures as well as to analyze and explain the sequence of intermediary compound formation.

EXPERIMENTAL

The following materials were used in this work: calcium hydroxide Ca(OH)₂ (the purity is 98 %, the product of ACROS ORGANICS, Belgium), industrial CaO (loss on ignition 23 %, Manufacturer Pigeon Chaux, Saint Pierre La Cour, FRANCE) and thermal silica densified - TSD (amorphous silica > 86 %, carbon content < 5.4 %, pH = 6.3, surface area – 120 m²/g, obtained from Nantes).

Two series of samples, each being made with different forms of CaO and SiO₂, were used in the experimental tests. The molar ratio of primary mixtures was CaO/SiO₂ equal to 1.0. Hydrothermal synthesis has been carried out under the saturated steam pressure at temperatures of 90, 110, 130, 150 and 175°C; the duration of isothermal curing was 2, 8, 24 or 72 hours. After synthesis, samples were removed from the teflon cells and were transferred to an air conditioned chamber with relative humidity of 55 % and temperature of 20°C and sieved through a sieve with a mesh width of 50 μ m.

The XRD data were collected with Philips PW 3710 X-ray diffractometer with Bragg–Brentano geometry using Ni-filtered Cu K_a radiation, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2–60° (2 θ) in steps of 2 θ = 0.02°.

SEM (JEOL-JSM-6301F) of the samples was performed using an accelerating voltage of 9 kV and a working distance of 15 mm.

FT–IR spectra has been carried out with the help of spectrometer Perkin Elmer FT–IR system Spectrum X. Specimen were prepared by mixing 1 mg of the sample with 200 mg of KBr. The spectral analysis was performed in the range of 4000-400 cm⁻¹ with spectral resolution of 1 cm⁻¹.

RESULTS AND DISCUSSION

It was determined that using SiO₂ component - thermal silica densified, the formation of calcium silicate hydrates proceeds very difficult to compare with amorphous silica [21-24]. In Ca(OH)₂–TSD–H₂O mixture at 90°C together with C–S–H(I) (*d*-spacing: 0.302; 0.179; 0.168 nm) and CaCO3 (*d*-spacing: 0.383; 0.302; 0.249; 0.228; 0.209; 0.192; 0.187 nm) as well unreacted Ca(OH)₂ remained (*d*-spacing: 0.487; 0.310; 0.262; 0.192; 0.179; 0.168 nm) (Figure 1, curve 1). It should be underlined that the carbonation appeared when the products were dryed in air conditionned chamber. It is presumable that one of the main reasons is that TSD contains quite a large quantity of carbon which impedes the reaction between Ca²⁺ and Si⁴⁺ ions [24].





Figure 1. X-ray diffraction patterns of synthesis products at 90°C in the $Ca(OH)_2$ -TSD-H₂O mixture. Indexes: C - C-S-H(I), P - Ca(OH)₂, Ka - calcite.



Figure 2. SEM micrographs of synthesis products in the $Ca(OH)_2$ -TSD-H₂O mixture when duration of hydrotermal treatment at 90°C, h: a) 2, b) 72.

Upon extending the duration of synthesis (till 72 hours), in the products the quantity of unreacted $Ca(OH)_2$ decreases because the intensity of the main diffraction peak (*d*-spacing: 0.487) diminishes too (Figure 1, curves 2-4).

SEM analysis data show that within 2 h of isothermal curing also silica fume-TSD completely does not react because the irregular plates typical of it dominate in the products (Figure 2a). Meanwhile, in the products



Figure 3. X-ray diffraction patterns of synthesis products at 150° C in the Ca(OH)₂–TSD–H₂O mixture. Indexes: C - C–S–H(I), P - Ca(OH)₂, Ka - calcite.

within 72 hours of hydrothermal treatment amorphous, with no definite crystal structure aggregations typical for a low crystalline degree C–S–H(I) were already identified (Figure 2b).

By increasing the temperature of synthesis (up to 150°C), the composition of C–S–H(I) and a sequence of reaction products were not affected in the Ca(OH)₂–-TSD–H₂O mixture. At 110, 130 or 150°C the same compounds were formed as at 90°C: C–S–H(I), CaCO₃ and Ca(OH)₂ (Figure 3).

SEM analysis showed that by increasing the temperature of isothermal curing, after 72 h at $110-150^{\circ}$ C the stucture of C–S–H(I) vary from the common fibrous type to irregular grains/aggregates forming a reticular network (Figure 4).

At 175°C, the XRD data showed that almost all Ca(OH)₂ reacted and well-crystalline C-S-H(I) were formed (Figure 5a). The results of X-ray diffraction analysis were confirmed by FT-IR and SEM data. A broad absorption bands at 475; 673; 976; 1640; 3450 cm⁻¹ are typical for C–S–H(I). The broad band centered at 1117 cm⁻¹ is attributed to asymmetric stretching frequency of Si–O–Si, the band centered at 798 cm⁻¹ is due to symmetric stretching of Si-O-Si, and the band at 475 cm⁻¹ is due to the bending frequency of O–Si–O. The frequencies of the Si-O-Si bands are an indication of the overall degree of polymerization of the silica network. In general, a lower frequency will correspond to a lower degree of polymerization. Also the presence of calcite impurities was indentified with an absorption bands at 713; 874; 1428 cm⁻¹ (Figure 5b). In results of scanning electron micrographs, well-crystalline aggregates of C–S–H(I) plates can be seen (Figure 6).

Thus, in $Ca(OH)_2$ -TSD-H₂O mixture, thermal silica densified grains impeded synthesis of C–S–H(I). It should be underlined that by increasing synthesis temperature and prolonging the duration of synthesis, the quantity of unreacted Ca(OH)₂ sligthly decreases. As it results from the data shown in Figure 7 at low temperature (90°C) almost half of Ca(OH)₂ does react during



Figure 4. SEM micrographs of synthesis products in the $Ca(OH)_2$ -TSD-H₂O mixture when duration of hydrotermal treatment at 110°C (a), 130°C (b) and 150°C (c) is 72 h.

72 hours. The further reduction of its quantity depends on temperature of hydrothermal curing. At higher temperatures (175°C), Ca(OH)₂ reacts considerably more quickly and about 75–80 % of it is bound during 72 hours of isothermal curing. It was noticed that the last amount of Ca(OH)₂ reacts very slowly.

Meanwhile, it is known that CaO reacts more quickly with amorphous SiO_2 components than $Ca(OH)_2$. It is possible that formation process of C–S–H proceeds better in CaO–TSD–H₂O system than in Ca(OH)₂–TSD–H₂O.

It was determined that formation process of calcium silicate hydrates proceeds faster in CaO–TSD–H₂O system than in Ca(OH)₂–TSD–H₂O only at higher temperature because curves of the X-ray diffraction analysis of the synthesized compounds show that similar amounts of C–S–H(I), portlandite and CaCO₃ formed irrespective of synthesis temperature (90, 110, 130, 150°C) and duration (4, 8, 24, 72 h) because the intensities of the main diffraction peaks typical for them are almost analogous (Figure 8). Moreover, upon extending the duration or temperature of synthesis, in the products the quantity of unreacted Ca(OH)₂ sligthly decreases because the intensity of the main diffraction peak (*d*-spacing: 0.490) decreases too (Figure 8).

The data of SEM analysis presented that in the temperature range from 90° C to 150° C the overal morphology of C–S–H(I) varies from the common fibrous type to irregular plates (Figure 9).



Figure 6. SEM micrographs of synthesis products in the $Ca(OH)_2$ -TSD-H₂O mixture when duration of hydrotermal curing at 175°C is 72 h.



Figure 5. X-ray diffraction patterns (a) and FT-IR spectra (b) of synthesis products at 175° C in the Ca(OH)₂–TSD–H₂O mixture. Indexes: C - C–S–H(I), P - Ca(OH)₂, Ka - calcite.

It should be underlined that at 175°C unexpected results were obtained. The accumulation of two morphologous crystals can be seen in SEM micrographs: C–S–H(I) characteristic irregular shape crystals and long, needle/plate shape xonotlite crystals that are formed as on C–S–H(I) grains and in the interlayers between them (Figure10).

The formation of xonotlite is confirmed by XRD studies only after 72 h at 175° C: the main peak with *d*-spacing: 0.703 nm which is specific to xonotlite was identified (Figure 11, curve 4, *d*-spacing: 0.703; 0.426; 0.364; 0.271; 0.250; 0.228 nm).

Obtained results confirmed that CaO reacts more quickly with amorphous SiO_2 component (TSD) than $Ca(OH)_2$. It should be underlined that dissociation of $Ca(OH)_2$ depends on temperature of hydrothermal curing. At 175°C, $Ca(OH)_2$ reacts considerably rapidly and about 90 % of it is bound during 72 hours of isothermal curing (Figure 12).

Thus, in CaO–TSD–H₂O system at the temperature range from 90°C to 175°C, the sequence of compounds to be formed during the synthesis looks as follows:

raw
materials
$$CaCO_3$$
 $CaCO_3$
 $Ca(OH)_2 \rightarrow Ca(OH)_2 \rightarrow$ $CaCO_3$
 $CaCO_3$
xonotlite
 $C-S-H$ gel $C-S-H(I)$

CONCLUSIONS

- It was determined that SiO₂ component thermal silica densified has negative influence on the formation of calcium silicate hydrates. It should be underlined that CaO reacts more quickly with thermal silica densified than Ca(OH)₂. Moreover, the reactivity of Ca(OH)₂ depends on temperature of hydrothermal curing.
- 2. It was estimated that the increment of temperature significantly influences the stability, morphology and crystalline degree of C–S–H(I) in the temperature range from 90°C to 175°C. The overall morphology of C–S–H vary from the common fibrous type to irregular grains forming a reticular network.
- 3. Ca²⁺ containing component (Ca(OH)₂, CaO) change the composition of intermediate and final products of the synthesis. In the mixtures with Ca(OH)₂, intermediary and final compound is C–S–H(I) in different crystalline degree. Meanwhile, in the mixtures with CaO, the main intermediary compound is C–S–H(I) and the main product is xonotlite. Moreover, in both mixtures calcite prevails at the beginning of the synthesis and remains in the products almost in all explored conditions.



Figure 7. Intensity of main peak (*d*-spacing: 0.490 nm) of $Ca(OH)_2$ at different temperature and duration of synthesis in the $Ca(OH)_2$ -TSD-H₂O mixture.

Ceramics - Silikáty 53 (2) 81-87 (2009)



Figure 8. X-ray diffraction patterns of synthesis products at 150° C in the CaO–TSD–H₂O mixture. Indexes: C - C–S–H(I), P - Ca(OH)₂, Ka - calcite.



Figure 9. SEM micrographs of synthesis products in the CaO–TSD– H_2O mixture when duration of hydrotermal treatment at 90°C (a), 110°C (b), 130°C (c) and 150°C (d) is 72 h.



Figure 10. SEM micrographs of synthesis products in the CaO–TSD–H₂O mixture when duration of hydrotermal curing at 175°C is 72 h.

Acknowledgement

The authors express their thanks to Joseph Le Lannic, CMEBA Universite de Rennes, for his assistance with scanning electron microscopy.

References

- 1. Richardson I. G.: Cem.Concr.Res. 38, 137 (2008).
- Chen J. J., Thomas J.J., Taylor H. F. W., Jennings H. M.: Cem.Concr.Res. 34, 1499 (2004).
- 3. Nonat A.: Cem.Concr.Res. 34, 1521 (2004).
- Black L., Garbev K., Beuchle G., Stemmermann P., Schild D.: Cem.Concr.Res. 36, 1023 (2006).
- 5. Hartmann A., Buhl J.-Ch., Breugel K.: Cem.Concr.Res. 37, 21 (2007).
- 6. Garbev K.: Ph. D. Thesis, Forschungszentrum Karlsuhe GmbH, Karlsruhe, (2004) (In German).
- Zhang X., Chang W., Zhang T., Ong C.K.: J. Am. Ceram. Soc. 83, 2600 (2000).
- 8. Richardson, I.G.: Cem.Concr.Res., 34, 1733 (2004).
- 9. Taylor H. F. W.: J.Chem.Soc. 36, 82 (1950).

- 10.Sun G. K., Young J. F., Kirkpatrick R. J.: Cem.Concr.Res. 36, 18 (2006).
- 11. Jennings H.M.: Cem.Concr.Res. 38, 275 (2008).
- 12.Constantinides G., Ulm F. J.: J.Mech.Phys.Solids 55, 64 (2007).
- Pellenq R. J. M., Lequeux N., Van Damme H.: Cem.Concr. Res., 38, 159 (2008).
- 14.Mohan K., Taylor H. F. W.: J.Am.Ceram.Soc. 64, 177 (1981).
- 15.Gard J. A., Howison J. W., Taylor H. F. W.: Mag.Concr. Res., 11, 151 (1959).
- Mitsuda T., Kobayakawa S., Toraya H.: Proc. 8th International Congress on the Chemistry of Cement, Vol. 2, p. 160, Rio de Janeiro 1986.

- 17.Sugiyama D., Fujita T.: Cem.Concr.Res., 36, 227 (2006).
- Babushkin V. I., Matveev G. M., Mchedlow-Petrossyan O. P.: *Thermodynamics of Silicates* (in Russian), Stroyizdat, Moscow, Russia, 1962.
- Kurdowski W., Nguyen T. T., Proceedings 9th ICCC, National Council for Cement and Building Materials, New Delhi 1992.
- 20.Shaw S., Henderson C. M. B., Clark S. M.: Amer.Mineral. 87, 553 (2002).
- 21. Jauberthie R., Temimi M., Laquerbe M.: Cem.Concr.Res. 26, 1335 (1996).
- 22. Siauciunas R., Baltakys K.: Cem. Concr. Res. 34, 2029 (2004).
- 23. Shaw S.: Ph. D. Thesis, University of Manchester, 1999.
- 24.Baltakys K., Jauberthie R. Siauciunas R., Kaminskas R.: Materials Science-Poland 25, 663 (2007).
- 25. Baltakys K., Siauciunas R.: Ceramics-Silikáty 51, 106 (2007).



Figure 11. X-ray diffraction patterns of synthesis products at 175°C in the CaO–TSD–H₂O mixture. Indexes: C - C–S–H(I), P - Ca(OH)₂, Ka - calcite, X - xonotlite.



Figure 12. Intensity of main peak (*d*-spacing: 0.490 nm) of $Ca(OH)_2$ at different temperature and duration of synthesis in the CaO–TSD–H₂O mixture.