Materials Science-Poland, Vol. 25, No. 3, 2007

Influence of modification of SiO_2 on the formation of calcium silicate hydrate

K. BALTAKYS[1*], R. JAUBERTHIE[2], R. SIAUCIUNAS[1], R. KAMINSKAS[1]

[1]Department of Silicate Technology, Kaunas University of Technology, Radvilenu 19, LT – 50270 Kaunas, Lithuania

[2]Department of Civil Engineering, INSA, 20 Av. des Buttes de Coësmes, CS 14315, 35043 Rennes, France

Interactions of $Ca(OH)_2$ with various modifications of SiO_2: amorphous (Hi-Sil, TSD) or crystalline (quartz) silica were established. The molar ratio of primary mixtures CaO/SiO_2 was 0.5. The samples were cured in a vapour chamber (20 ºC, 100% humidity) for 7 and 28 days. The products were characterized by X–ray diffraction, thermogravimetry, differential scanning calorimetry, Fourier-transform infrared and scanning electron microscopy analysis. SiO_2 modification used had a decisive influence on the processes of formation of calcium silicate hydrates. In the mixture with amorphous SiO_2, $Ca(OH)_2$ reacted completely during 7 days of synthesis, while large quantity of $Ca(OH)_2$ remained unreacted even after 28 days when quartz was used. It was found that in the $Ca(OH)_2$–amorphous SiO_2–H_2O system, after a 28-day exposure, the surface of SiO_2 globules was totally covered with well-crystalline C-S-H(I) plates. Moreover, in the samples with quartz, only the gaps between quartz crystals were filled with C-S-H(I).

Key words: *calcium silicate hydrate; crystalline SiO_2; silica fume; Portland cement; X-ray diffraction*

1. Introduction

In recent times, the term pozzolan has been extended to cover all siliceous /aluminous materials which in finely dispersed form and in the presence of water, react with calcium hydroxide (CH) to form compounds with cementitious properties. This generalized definition covers waste products such as fly ash, rice husk ash, silica fume (SF) [1–4].

Silica fume is a by-product of silicon and ferro-silicon industries. It is formed by condensation of SiO_2 from the vapour phase. SF occurs as near-perfect spheres with diameters ranging from 20 to 500 nm. Typically, 85–95% of SF has the form of amor-

*Corresponding author, e-mail: kestutis.baltakys@ktu.lt

phous silica [5–7] with various impurities, such as an ultra fine by-product of the silicon metal refining industry.

As a pozzolana, SF reacts with calcium hydroxide liberated by the hydrolysis of C_3S and C_2S of Portland cement in the following reactions [8]:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \quad (1)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \quad (2)$$

$$3CH + 2S \rightarrow C_3S_2H_3 \quad (3)$$

However, there are still a lot of questions concerning the role of pozzolans. The most commonly discussed mechanisms are the following [9]: (a) pozzolans reduce permeability, thereby preventing the ingress of water and transport of alkali and hydroxyl ions; (b) pozzolans increase strength and stiffness, resulting in better resistance to cracking and less expansion; (c) replacing a portion of cement with a less-alkaline pozzolanic material decreases the total amount of alkali present; and (d) pozzolans react with calcium hydroxide to form calcium silicate hydrate (CSH) with a low CaO/SiO_2 ratio. Formation of CSH depletes CH and the low C/S ratio enables the entrapment of alkalis, both of which reducing the amount of hydroxyl ions available to participate in the alkali–silica reaction.

The addition of SF to cement paste has been shown to give rise to high early strengths, although the mechanisms by which SF operates are unclear. Three principal types of interactions have been suggested:

1. SF particles cause pore blockage in the hydrating cement, which makes the hydrating gel structure more dense [6].

2. Pozzolanic reactions occur between the silica-rich SF particles and the portlandite, which is a by-product of Portland cement hydration [10].

3. SF particles act as nucleation sites for cement hydration, accelerating the process [11].

Addition of SF enhances the rate of cement hydration and accelerates both C_3S and C_3A hydration during the first few hours [12].

Calcium silicate hydrates have a vital influence on the characteristics of cement paste. Due to their morphology, CH are relatively weak, brittle and not cementitious. Moreover, the CSH phase formed by a pozzolanic reaction has a microscopic morphology similar to that developed by the hydration of the C_3S and C_2S found in Portland cement [13]. When silica fume is added to fresh concrete, it chemically reacts with the CH to produce additional CSH. The benefit of this reaction is two-fold: increased compressive strength and chemical resistance [14].

According to the collected reference data, the properties of hardening concrete with SF additive depends on CH reaction and SF kinetics parameters (the rate of reaction, advancement of reaction, etc.).

In this work, the presented data were obtained by performing syntheses of portlandite with various modifications of SiO_2: amorphous (Hi-Sil, TSD) or crystalline (quartz) silica under normal conditions.

2. Materials and methods

The following materials were used in this work: calcium hydroxide $Ca(OH)_2$ (Industrial lime: loss of ignition 23%, Manufacturer Pigeon Chaux, Saint Pierre La Cour, France); two different silica fumes (Hi-Sil 255C-D obtained from PPG (amorphous silica > 87%, crystalline silica < 0.01%, Na_2SO_4 < 2%, pH = 6.3, surface area – 180 m^2/g) and thermal silica densified – TSD (amorphous silica > 86%, carbon content < 5.4%, pH = 6.3, surface area – 120 m^2/g); quartz (from Millisil Sifraco).

Two series of samples, each being made with different SiO_2 and $Ca(OH)_2$, were used. The molar ratio of primary mixtures of CaO/SiO_2 was 0.5. The samples were cured in a vapour chamber (20 ºC, 100% humidity) for 7 and 28 days. Then, they were removed from the teflon cells and transferred into an air-conditioned chamber with relative humidity of 55% at 20 ºC, and sieved through the sieve No. 008. The products of the synthesis were characterized by X-ray powder diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetry (TG), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) methods.

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

Simultaneous thermal analysis (STA: differential scanning calorimetry – DSC and thermogravimetry – TG) was also employed for measuring the thermal stability and phase transformations of the synthesized products at a heating rate of 15 ºC/min, the temperature ranged from 30 ºC up to 1000 ºC under the ambient atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx with ceramic sample handlers and crucibles of Pt-Rh. SEM (JEOL-JSM-6301F) analysis of the samples was performed using an accelerating voltage of 9 kV and a working distance of 15 mm.

FT-IR spectra analysis was carried out with a spectrometer Perkin Elmer FT–IR system Spectrum X. The specimens 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}.

3. Results and discussion

FT-IR studies were conducted to identify differences of interaction of $Ca(OH)_2$ with various modifications of SiO_2: amorphous (Hi-Sil, TSD) or crystalline (quartz)

silica. The infrared spectra of the products after 7 and 28 days of hydrothermal curing at 20 ºC are shown in Fig. 1.

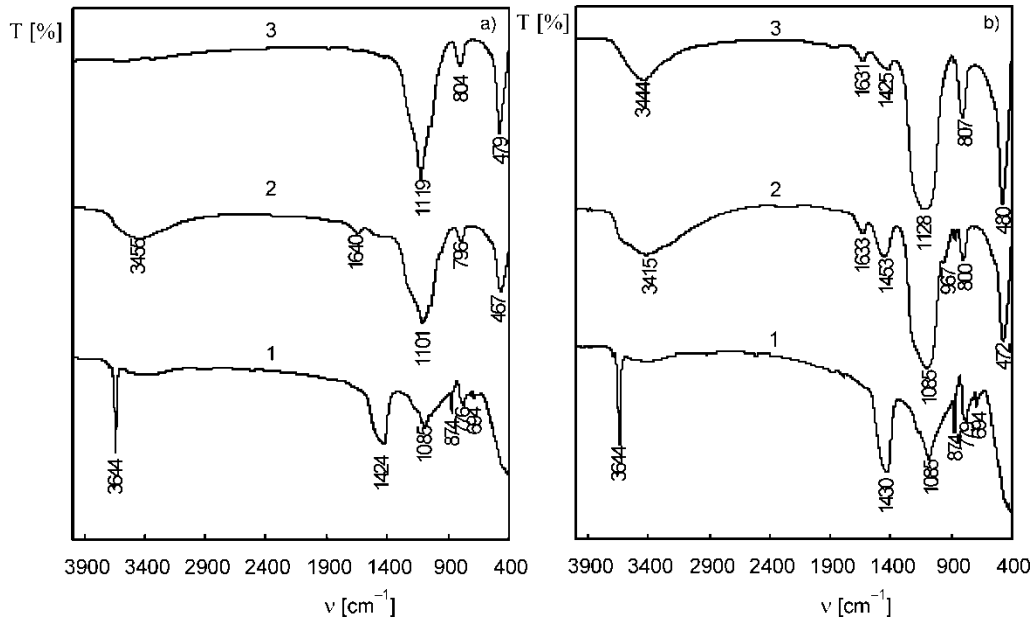

Fig. 1. IR spectra of products of the synthesis; duration of hydrothermal curing at 20 ºC: a) 7 days, b) 28 days; SiO_2 modifications: 1 – quartz, 2 – Hi-Sil, 3 – TSD

In the $Ca(OH)_2$–quartz–H_2O system, a broad absorption band at 3644 cm^{-1} characteristic of portlandite [15, 16] was observed. The band was clearly visible in both reactions products after 7 and 28 days of exposure (Fig. 1a, b, curve 1). Also, the presence of calcite ($CaCO_3$) impurities was identified with IR absorption bands at 874 and 1424 cm^{-1}.

In the mixtures with amorphous SiO_2 (Hi-Sil or TSD), just after 7 days of exposure the portlandite was not observed (Fig. 1a, curves 2, 3). This is the result of the reaction between CH and SiO_2 when calcium silicate hydrates are formed. The most significant infrared spectra of C-S-H contain a characteristic set of bands in the range 400–1200 cm^{-1}. The broad band centred at 1101 cm^{-1} is attributed to asymmetric stretching frequency of Si–O–Si, the band centred at 796 cm^{-1} is due to symmetric stretching of Si–O–Si, and the band at 467 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 corresponds to a lower degree of polymerization. Thus, one can speculate that the degree of polymerization of reaction products using Hi-Sil is lower compared to TSD because in the latter material corresponding absorption bands are located at 1119, 804, 479 cm^{-1}. As in the previous spectra, these bands become sharper and more intense with increasing reaction time (Fig. 1b). After 28 days of synthesis, only in the samples with Hi-Sil the band (ν_3 SiO_4) characteristic of C-S-H at 967 cm^{-1} [15, 16] was observed (Fig. 1b,

curve 2). A broad band, present in each spectrum around 1630 cm^{-1}, is associated with deformation vibrations δ(OH) and together with ν(OH) stretching vibrations at 3435 cm^{-1}, the presence of water in the samples can be concluded due to humidity. This assumption could be proved by DSC-TG measurement.

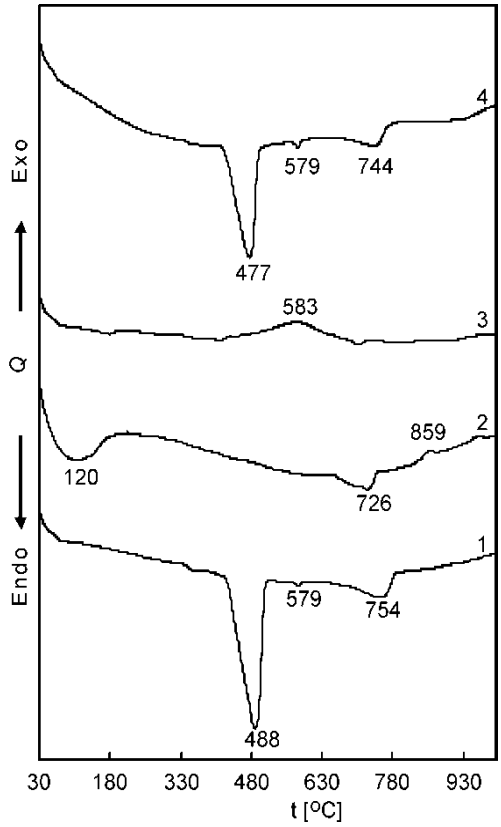

Fig. 2. DSC-TG curves for the following SiO_2 modifications and durations of hydrothermal curing at 20 ºC: 1 – quartz, 7 days; 2 – Hi-Sil, 7 days; 3 – TSD, 7 days; 4 – quartz, 28 days

The results of thermal analyses confirm the IR data. The endothermic peak in the range 475–485 ºC corresponds to the decomposition of $Ca(OH)_2$. This peak is clearly visible in the curves of the samples with quartz after 7 and 28 days of syntheses (Fig. 2, curves 1, 4). Moreover, this endothermic peak is not observed in any DSC curves of the samples with amorphous SiO_2 (Fig. 2, curves 2, 3).

X-ray diffraction analysis confirms that prolonging the duration of synthesis increases the quantity of semi-crystalline C-S-H(I) phase in the products and shows that the reaction proceeds more intensively in the $Ca(OH)_2$–Hi-Sil–H_2O mixture. The XRD data showed the presence of amorphous silica after 7 days of exposure (Fig. 3a, curves 1, 2) or quartz (Fig. 3a, curve 1) and only in the $Ca(OH)_2$–Hi-Sil–H_2O mixture semi-crystalline calcium silicate hydrate – C-S-H(I) can be seen (Fig. 3a, curve 2).

In the mixture with quartz, both after 7 days and 28 days, the main peak of $Ca(OH)_2$ was clearly visible (Fig. 3a, curve 1, *d*-spacing – 0.493, 0.262, 0.179 nm). At

the same time, this compound was not found in the mixture with amorphous silica (Hi-Sil, TSD) (Fig. 3a, curves 2, 3). After 28 days, the distinctly apparent peaks characteristic of C-S-H(I) were found in all samples. The most intensive peak was found in the mixture with Hi-Sil (Fig. 3b, curve 2).

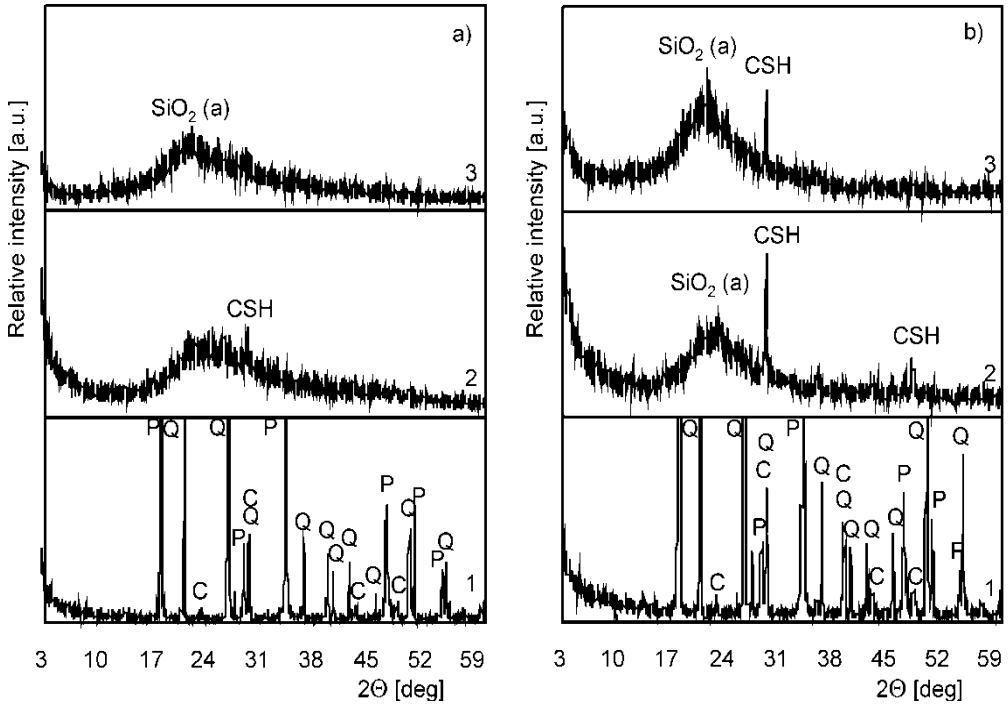

Fig. 3. X-ray diffraction patterns of the products of the synthesis; the duration of hydrothermal curing at 20 ºC: a) 7 days, b) 28 days; SiO_2 modifications: 1 – quartz, 2 – Hi-Sil, 3 – TSD; CSH – calcium silicate hydrates, P – portlandite, C – calcite, Q – quartz, SiO_2 (a) – amorphous silica

The same sequence of reactions was proved by SEM analyses. The SEM data show that the overall morphology of C-S-H can actually vary from the common fibrous type to irregular grains forming a reticular network [16].

In the mixture with amorphous SiO_2, after 7 days of synthesis, agglomerates of calcium silicate hydrates under the surface of silica globules were identified (Fig. 4a, b). $Ca(OH)_2$ reacts more quickly with Hi-Sil because the particles of this compound are significantly smaller than TSD (Fig. 4a). After prolonging the synthesis time to 28 days, well-crystalline CSH plates in the samples with Hi-Sil could be seen (Fig. 5a). The surface of SiO_2 globules was totally covered with these compounds.

At the same time, in the quartz samples only rudiments of CSH were observed after 7 days (Fig. 4c) and even after 28 days of synthesis only the gaps between quartz crystals were filled with CSH (Fig. 5b).

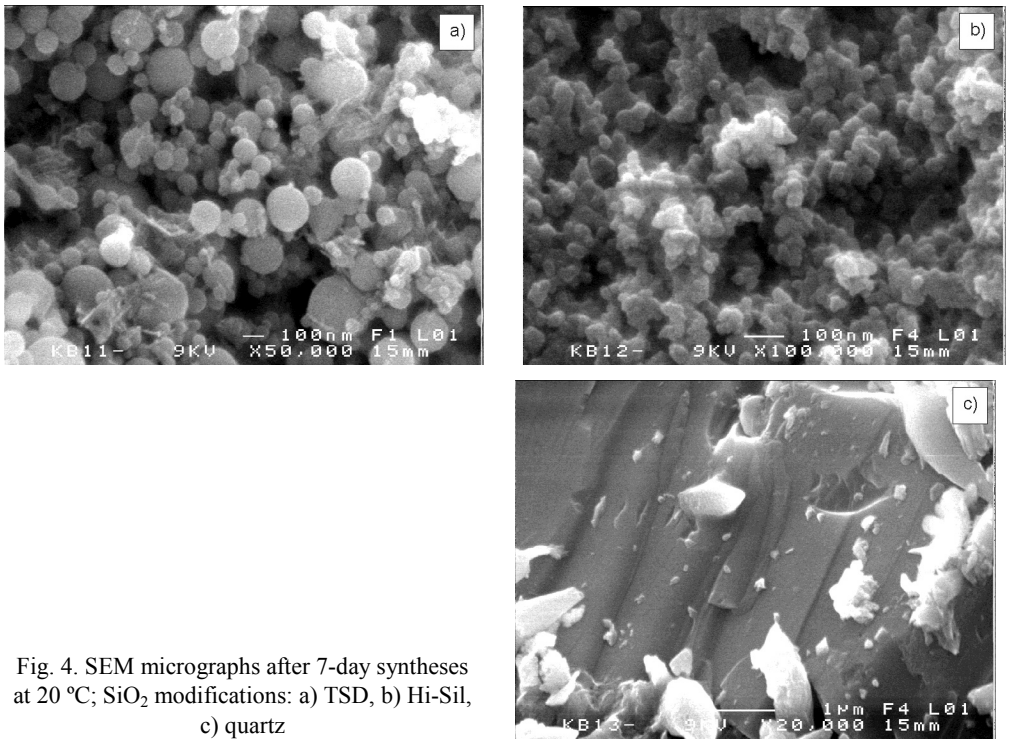

Fig. 4. SEM micrographs after 7-day syntheses at 20 ºC; SiO_2 modifications: a) TSD, b) Hi-Sil, c) quartz

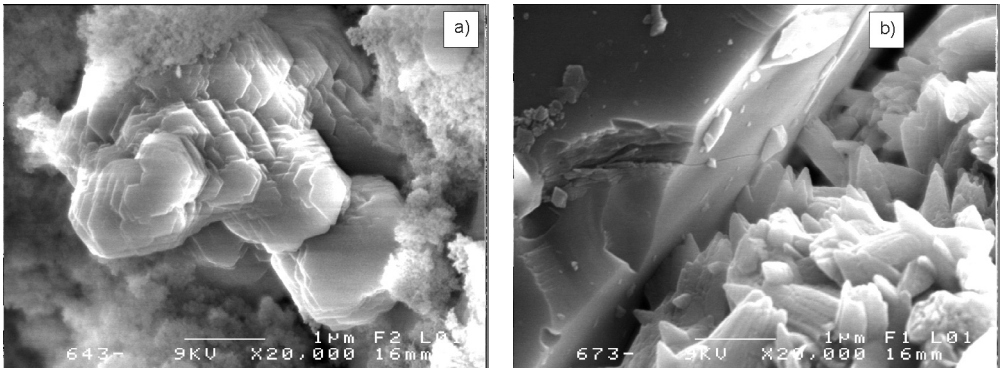

Fig. 5. SEM micrographs after 28-day syntheses at 20 ºC; SiO_2 modifications: a) Hi-Sil, b) quartz

4. Conclusions

• The phase compositions and properties of calcium silicate hydrates are strongly affected by crystallinity of SiO_2. In the mixture with amorphous SiO_2 (Hi-Sil or TSD), when primary mixture molar ratio CaO/SiO_2 was equal to 0.5, $Ca(OH)_2$ completely reacted during 7 days of synthesis at 20 ºC. When using quartz, a crystalline SiO_2 modification, large quantities of $Ca(OH)_2$ remained unreacted even after 28 days.

• In the $Ca(OH)_2$–amorphous SiO_2–H_2O system, after 7 days of synthesis, agglomerates of calcium silicate hydrates were formed covered by silica on the surface. After prolonging the synthesis to 28 days, the surface of SiO_2 globules was totally covered with well-crystalline C-S-H(I) plates.

• It was determined that, in the quartz samples, after 7 days only rudiments of C-S-H(I) were observed and even after 28 days of synthesis only the gaps between quartz crystals were filled with C-S-H(I).

References

[1] BEZERRA E.M., JOAQUIM A.P., SAVASTANO H., JOHN V.M., AGOPYAN V., Cem. Concr. Compos., 28 (2006), 555.
[2] KOHNO K., *Relative durability properties and strengths of materials containing finely ground silica and silica fume*, [in:] Proc. Third Int. Conf. *Use of Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, Vol. 2**,** American Concrete Institute, SP-114 (1989), p. 815.
[3] MARUSIN S.L., *The influence of length of moist curing time on the weight change behaviour and chloride permeability of concrete containing silica fume*, [in:] Proc. Third Int. Conf. *Use of Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, American Concrete Institute, SP-114 (1989), p. 924.
[4] MEHTA P.K., GJORV O.E., Cem. Concr. Res., 12 (1982), 587.
[5] RALPH K.I., *The Chemistry of Silica*, Wiley, New York (1979) pp. 21–29.
[6] BONEN D., KHAYAT K.H. Cem. Concr. Res., 25 (1995), 395.
[7] BABU K.G., PRAKASH P.V.S., Cem. Concr. Res., 25 (1995), 1273.
[8] APPA RAO G., Cem. Concr. Res., 33 (2003), 1765.
[9] DUCHESNE J., BÉRUBÉ M.A., Cem. Concr. Res., 24 (1994), 73.
[10] MITCHELL D.R.G., HINCZAK I., DAY R.A., Cem. Concr. Res., 28 (1998), 1571.
[11] KIRKBRIDGE T.W., *Condensed Silica Fume in Concrete*, FIP State of Art Report, [in:] FIP Commission Thomas Telford, London (1988).
[12] LARBI J.J., FRAAY A.L.A., BIJEN J.M., Cem. Concr. Res., 20 (1990), 506.
[13] CHENG YI-H., FELDMAN R.F., Cem. Concr. Res., 15 (1985), 585.
[14] MAROPOLOU A., CAKMAK A., LABROPOULOS K.C., VAN GRIEKEN R., TORFS K., Cem. Concr. Res., 34 (2004), 1.
[15] RAMACHANDRAN V.S., BEAUDOIN J.J., *Handbook of Analytical Techniques in Concrete Science and Technology*, William Andrew Publishing/Noyes, New York, 2001.
[16] TAYLOR H.F.W., *Cement Chemistry*, 2nd Ed., Thomas Thelford, London, 1997.

Received 3 January 2006
Revised 30 January 2007