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## Examinations of the structure of highly polymerized alkali containing C-S-H phases

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Cement is an inorganic hydraulic binder widely used in civil engineering. By the reaction of cement with water calcium-silicate-hydrate (C-S-H) gel is the principal hydration product [1]. For example, building materials based on Portland cement could contain up to 70 wt% C-S-H gel. Therefore, the structure of the C-S-H gel is responsible for the mechanical properties of the hardened cement paste. The chemical composition of C-S-H gel varies between the molar CaO/SiO<sub>2</sub> (C/S) ratio of 0.5 in older and partly carbonated hardend cement paste and 2.2 in fresh ones. Reaction products (alkali containing C-S-H gels) of the deteriorative alkali-silica-reaction (ASR) show an even lower Ca content. Additionally, these gels have a significant amount of alkalis. Their formation processes and the reaction mechanism of ASR are still unknown and a subject of investigation.

To get insights into the structure and formation processes of alkali-C-S-H gels, samples with different chemical compositions have been synthesized with the agate-ball milling technique. A part of the gels was converted into their crystalline analogues by hydrothermal treatment. Due to their low crystallinity the gels were investigated with complementary spectroscopic and diffraction methods. Synchrotron based measurements at the diffraction-, XAFS- and IR-beamlines at ANKA (Ångströmquelle Karlsruhe) were performed. By comparison of the gels and crystalline alkali-C-S-H with XAFS measurements at the Ca absorption edge, it turned out that the Ca environment is stronger affected upon hydrothermal treatment in Ca poor samples than in samples with a higher C/S ratio. Similar results for the K environment were achieved from XAFS measurements at the K absorption edge. Data from IR spectroscopy show distinct changes in the region of Ca polyhedra vibrations around 240 cm<sup>-1</sup> [2]. This result is in good agreement with the XAFS measurements.

To point out the role of water in the gels structure the dehydration of C-S-H and alkali-C-S-H was followed in situ with IR-microscopy and the total water loss was analyzed with DTA/TG. The IR data reveal a structural reorganization of the gel. Especially the bands in the Si-O-Si stretching region show distinct changes during the drying process whereas bands attributed to Ca polyhedra vibrations remain largely unchanged.

[1] Taylor, H.F.W. (1964): The Chemistry of Cements. Academic Press, London, New York. p. 168.

[2] P. Yu, R.J. Kirkpatrick, B. Poe, P.F. McMillan, X. Cong (1999): Structure of Calcium Silicate Hydrate (C-S-H): Near-, Mid-, and Far-Infrared Spectroscopy. J. Am. Ceram. Soc.

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## An unusual phase transition Ca<sub>2</sub>[SiO<sub>3</sub>(OH)](OH) - Ca<sub>6</sub>[Si<sub>2</sub>O<sub>7</sub>][SiO<sub>4</sub>](OH)<sub>2</sub> (dellaite) as revealed by single crystal IR and X-ray powder diffraction

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To lower the CO<sub>2</sub> emission in cement production low energy cements are developed. A promising method is hydrothermal synthesis of α-Ca<sub>2</sub>[SiO<sub>3</sub>(OH)](OH) followed by calcination. Alpha-Ca<sub>2</sub>[SiO<sub>3</sub>(OH)](OH) or α-C<sub>2</sub>SH is a calcium silicate hydrate present in hydrothermal treated cement pastes and concrete. HT-XRD data show for the first time formation of Ca<sub>6</sub>[Si<sub>2</sub>O<sub>7</sub>][SiO<sub>4</sub>](OH)<sub>2</sub> (dellaite) as intermediary product during dehydration of α-C<sub>2</sub>SH. According to [1] dellaite is formed only under pressures higher than 345bar. <sup>29</sup>SiNMR confirms the polymerization of the silicate structure showing presence of Q<sup>1</sup> Si-units typical for dellaite. IR absorption bands typical for the initial α-C<sub>2</sub>SH phase, e.g. librations of Si-bonded O-H between 600 and 700cm<sup>-1</sup>, Si-OH stretching at 1278cm<sup>-1</sup>, the doublet at about 2445 and 2872cm<sup>-1</sup> caused by H-bonds as well as the O-H stretching at 3447 and 3538cm<sup>-1</sup>, diminish and further disappear completely in the course of thermal treatment. At the same time, bands characteristic for dellaite appear in the IR spectra at 1050, 3574 and 3594cm<sup>-1</sup> after heating. The band at 1050cm<sup>-1</sup> is due to the new-formed Si-O-Si linkages ([Si<sub>2</sub>O<sub>7</sub>]-groups) in dellaite instead of the Si-OH termination of the isolated tetrahedra in α-C<sub>2</sub>SH. Synchrotron-IR maps recorded at the ANKA-IR beamline of α-C<sub>2</sub>SH heated in the range 340-450°C show dellaite domains in the core of the crystals. The rim consists of α-C<sub>2</sub>SH, which transforms to x-Ca<sub>2</sub>SiO<sub>4</sub> [2] at T>450°C. Dellaite coexists with x-Ca<sub>2</sub>SiO<sub>4</sub> up to 650°C, and transforms to β-Ca<sub>2</sub>SiO<sub>4</sub> and α'<sub>L</sub>-Ca<sub>2</sub>SiO<sub>4</sub> upon further heating. One interesting point to discuss is the mechanism of the phase transition of α-C<sub>2</sub>SH into dellaite. After our hypothesis this indicates an "autoclave effect" within a single crystal, where the water diffusion out of the crystal structure plays a decisive role by building some pressure inside the crystal high enough for dellaite to form. The dehydration of α-C<sub>2</sub>SH is a multi-stage process for the reason of different bond strengths of the OH groups. These belonging to the coordination sphere of Ca dehydrate at higher temperatures compared to the relatively weakly bonded OH groups coordinating the silicate tetrahedra. The dehydration of two isolated SiO<sub>3</sub>(OH) silicate tetrahedra could result in their condensation: 2[SiO<sub>3</sub>(OH)] - H<sub>2</sub>O → [Si<sub>2</sub>O<sub>7</sub>], which is the first step towards formation of dellaite. The whole equation for the phase transition of α-C<sub>2</sub>S into dellaite could be presented as follows: 3Ca<sub>2</sub>[SiO<sub>3</sub>(OH)](OH) - 2H<sub>2</sub>O → Ca<sub>6</sub>[Si<sub>2</sub>O<sub>7</sub>][SiO<sub>4</sub>](OH)<sub>2</sub>. We suggest that this reaction cannot be completed in the regions close to the rim of the crystals because of the missing steam pressure. For this reason we expect the formation of x-C<sub>2</sub>S to start along the crystal edges.

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