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The formation of 1.13 nm tobermorite under hydrothermal conditions: 1. The influence of quartz grain size within the system $CaO–SiO_2–D_2O$

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A B S T R A C T

The influence of grain size of quartz on the formation of 1.13 nm tobermorite in aerated autoclaved concrete was investigated by applying in-situ neutron diffraction. Experiments were performed at 210 °C/P_{sat} employing quartz of 8 μm and 16 μm, respectively. The results reveal changes in the reaction mechanism from solution control to diffusion control. The grain size of the quartz fraction clearly influences the occurrence of those changes. Based on those results an interpretation of former not clearly interpretable quenching experiments was performed. An interpretation using different reaction mechanisms for those experiments leads to a coherent picture of the reaction.

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1. Introduction

Calcium Silicate Hydrates (CSH-phases) are very rare in nature but one deploys their properties in several technical applications. Up to now the main scope lies in the production of steam cured building materials. For the fabrication of aerated autoclaved concrete (AAC),one of the most popular building materials in Europe for lightweight mode of construction, 1.13 nm tobermorite is the predominant phase. The evolved crystal texture mainly controls the mechanical and thermal properties of the product, like high pressure resistance and low thermal conductivity.

1.13 nm tobermorite crystallizes in a layered structure, stacked along [001] with a basal spacing of 1.13 nm. The average structure was described by Hamid [1] but the real structure was solved by Merlino

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et al. [2,3] which is based on two polytypic modification of orthorhombic and monoclinic symmetry leading to a disordered structure (O/D character). The common structural feature is characterized by infinite silicate double chains of a type called Dreierdoppelketten built up of condensed dreierketten (kinked to repeat at intervals of three tetrahedra) along [010]. The chains are intercalated by a Ca–O layer (portlandite layer) so the structure consists of a central layer of calcium octahedra which has silicate sheets on each side. The calcium octahedra share oxygens with the silicate tetrahedra, the distance between two edges in the calcium octahedral layer is about the same length as a silicate dreierketten unit. This type of structural unit is characteristic for most of all CSH-phases. In 1.13 nm tobermorite the compositae layers of one calcium and two silicate layers are bound together by an interlayer containing calcium ions and water molecules. The interlayer contains variable amounts of calcium so that charge balance is achieved by variation of hydrogen atoms bonded to the silicate chains. Therefore, the variable occupancy of calcium in these layers allows the Ca:Si ratio to vary from $Ca_5Si_6O_{16}(OH)_2 {}^*4H_2O$ ($C_5S_6H_5$) to $Ca_4Si_6O(OH)_2 {}^*2H_2O$ ($C_4S_6H_3$) [2,3]. In AAC, 1.13 nm tobermorite is close to the composition $Ca_5Si_6O_{16}(OH)_2 {}^*4H_2O$ and occurs in association with semi-crystalline CSH-phases CSH (I) and CSH (II) as minor components. In contrast to tobermorite these phases are highly disordered and display a wide range of compositions. They are classified by their Ca:Si ratio: CSH (I) with a Ca:Si ratio <1.5 and CSH (II) with a Ca:Si ratio >1.5 according to Taylor [4,5].

There has been a lot of work in this field aimed at understanding the formation mechanisms and growth kinetics of CSH-phases [e.g [6,7].]. But little quantitative data exist on the kinetics of 1.13 nm tobermorite formation. In addition there is no accordance on the nature of the reaction mechanism because some studies proposed being solution controlled and others being diffusion controlled as pointed out in detail by Klimesch et al. [8].

The reaction mechanism and kinetics of the formation of 1.13 nm tobermorite in the pure cement-free system $CaO–SiO_2–H_2O$ from lime, silica and water ($CaO + SiO_2 + H_2O$) under hydrothermal conditions were determined by quenching experiments at 180°–190°C/P_{sat} [5,6,9] and by an in-situ Neutron diffraction experiment [10] as well. Quenching experiments reveal the disadvantage of missing data for the early evolution of phases in time and have prevented a quantitative kinetic description so far.

The formation of tobermorite is, in addition to reaction temperature and the amount of Al in the initial mixture, mainly affected by the grain size of quartz [8,11] .Therefore, the major aim of this investigation was to determine reaction mechanism and kinetics of the formation of 1.13 nm tobermorite under hydrothermal conditions as a function of the grain size of quartz. Experiments were conducted at 210 °C employing quartz with a grain size of 8 μm and 16 μm, respectively. In order to avoid quenching effects in short-time runs the experiments were conducted at in-situ conditions and data will be collected by means of neutron diffraction with the HAND apparatus [12].

2. Experimental

In-situ experiments under hydrothermal conditions were conducted at 210 °C under saturation pressure and within a time-range of up to 10 h by applying a hydrothermal autoclave cell for neutron diffraction HAND [12] at the D20 powder diffractometer of the high-flux neutron-source ($4.2^* 10^7$ n cm^{-2} s^{-1}) at Institute Laue-Langevin (ILL), Grenoble. In order to obtain neutron diffraction spectra with a low background noise, hydrogen-free substances have to be used, and contact of the materials with humidity must be minimized. Thus the experiments were carried out with heavy water (D_2O) instead of H_2O as hydrous reactant. To control the influence of D_2O on the kinetics of the tobermorite-forming reaction two preliminary quenching experiments were conducted in cold seal pressures vessel at 190°C/Psat for 8 h, using D_2O and H_2O as hydrothermal fluid, respectively. Analyses of the final products by X-rax diffraction demonstrate no differences between both runs as indicated by similar phase assemblages and phase amounts.

Pure SiO_2, CaO and D_2O were used as starting materials in order to determine the reaction kinetics in the simple system $CaO–SiO_2–D_2O$ according to the reaction:

$$5CaO + 6SiO_2 + 5H_2O \Rightarrow Ca_5Si_6O_{16}(OH)_2 * 4H_2O \quad (1)$$

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