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Hydrothermal synthesis of CSH-phases (tobermorite) under influence of Ca-formate

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ABSTRACT

The influence of Ca-formate ($C_2H_2CaO_4$) on the crystallization of the CSH-phase 11 Å tobermorite was investigated under hydrothermal conditions at 200 °C in a wide CaO/SiO_2 range of 0.67–1.24. Besides clarifying questions on acceleration or retarding of CSH formation at high Ca-formate contents even a study on the effect of this salt addition on the crystal morphology was a main objective of the present work. All experiments were performed using fine grained SiO_2 powder (P) or coarse grained quartz sand (S) as silicate source. The reactions were followed by XRD, SEM/EDX and FTIR. Except the reaction at lowest amount of formate (0.43 g), where only a very small effect on the crystallization rate was observed, higher salt concentrations were found to retard the reaction clearly. Here the reduction of the CSH-crystallization velocity and formation of tobermorite with a distinct character of the pre-phase CSH-I could be stated in each case. Its amount and crystal quality was not rigorously dependant on the inserted mass of Ca-formate in the 0.67–1.34 g range investigated here.

A strong influence on the morphology of the CSH-crystals was further detected already in the whole range of salt concentration, i.e. even at the low value of 0.43 g, examined in our experiments. Instead of the typical rod-like morphology of tobermorite formed without Ca-formate, a disturbed bent-needle-like morphology occurred at elevated formate concentrations. In contrast small compact crystals were observed at low amounts of Ca-formate.

Syntheses with quartz powder and quartz sand in principle yielded to comparable results concerning the retarding effect and the change of crystal morphology. As expected, the reaction rate of experiments with quartz sand was diminished in general, according to the lower specific surface of the sand grains, compared with the powder.

A change of the pH-value with marked influence on the solubility rate of the educts and the further course of reaction can be excluded as cause for the observed behavior. Further reasons, based on crystal growth under influence of adsorption of formate ions at specific crystal faces were discussed.

The improvement of knowledge on effects of additives on CSH crystallization will be of importance for future modifications of reaction processes of cement and concrete as well as steam hardened construction materials, where 11 Å tobermorite acts as the main binding agent.

1. Introduction

Under hydrothermal conditions of 160–200 °C and saturated steam pressure of 16 bar quartz, calcium hydroxide and water crystallize to calcium–silicate–hydrate phases (CSH-phases) [1–3]. The calcium silicate hydrate 11 Å tobermorite $Ca_5Si_6O_{17}\cdot 5H_2O$, the main binding agent in steam hardened building materials like lime sand stone, forms hydrothermally under kinetic control at temperatures around 180 °C and saturated vapor pressure from portlandite ($Ca(OH)_2$), quartz and water [1–3].

In the present paper the influence of the additive Ca-formate ($C_2H_2CaO_4$) on the crystallization of CSH-phases was investigated. It is known that additives can be retarders or accelerators for hardening reactions of buildings materials like cement and concrete. The action mechanism of retarders and accelerators is quite well understood for the latter materials and additives were applied in practice since long time [4–6]. For concrete a typical retarder like saccharate forms complexes with calcium ions. A strong influence on the whole mechanism of hardening results because of a time dependent failure of those calcium ions for CSH-phase formation [7]. Accelerators of setting period like aluminumsulfate are influencing the reactions of tricalciumaluminate for instance by higher rates of ettringite formation in the early hydratation process whereas hardening accelerators like calcium

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chlorite or calcium formate are promoting growth of CSH phases at later stage [4,8–10] Accelerating of the setting period but retarding of hardening has to be noticed in some cases too [11].

In contrast there is only a very few knowledge on the effects of additives during formation of CSH phases in steam hardened building materials like lime sand stones and autoclaved aerated concrete. In our former experimental study the addition of sucrose during tobermorite synthesis was studied [12]. The investigations of the system $CaO–SiO_2–C_{12}H_{22}O_{11}–H_2O$ at 200 °C and autogeneous pressure revealed sucrose as a retarder of tobermorite crystallization with relations to the effect of $C_{12}H_{22}O_{11}$ already known from its insertion in cement and concrete. Formation of saccharated lime and its secondary decomposition products caused a failure of calcium ions necessary for tobermorite crystallization [12].

In order to extent those investigations on the field of 11 Å tobermorite formation under the conditions of production of steam hardened building materials the aim of the present study was to examine the influence of the additive Ca-formate. Ca-formate acts as an accelerator for the hardening reactions of cement, as already mentioned above.

Ca-formate $Ca(HCOO)_2$, the Ca salt of the formic acid HCOOH [13], is a widespread admixture of cement causing an acceleration of the degree of hydration of C_3S [14,15]. It can be simply synthesized and is available from other processes of chemical industry in suitable amounts [13,15]. If Ca-formate will prove oneself to accelerate tobermorite formation with suitable crystal morphology an insertion of this salt could be of future interest for steam hardened building materials production process. Furthermore a usage of lower amounts of lime according to the partly substitution by Ca-formate is a step to reduce CO_2 emissions connected with lime production by calcite calcination. Energy saving seems possible too if lower reaction temperatures and/or reaction times could be revealed during steam hardening under addition of a suitable accelerator of CSH-formation.

Summarizing our aims we present an experimental study to clarify if the addition of Ca-formate favors or restricts the crystallization of 11 Å tobermorite with regular needle-shaped or batten-like morphology in larger amounts as in a salt-free synthesis. The question of formation of other Ca-consuming phases than 11 Å tobermorite ruled by the additive is of special interest in this context too, because under the conditions of production of steam hardened construction materials tobermorite is the metastable phase formed under kinetic control instead of the equilibrium phase Xonotlite [1–3]. The retrograde solubility of $Ca(OH)_2$ with increasing temperature is responsible for these non equilibrium conditions of tobermorite formation [1–3,16,17].

The experimental investigations of the present paper were performed in dependence of different mass ratios of Ca-formate, lime and quartz. The latter was inserted either as fine grained SiO_2 powder (P) or as coarse grained quartz sand (S).

2. Experimental

2.1. Syntheses

As in former experiments on CSH syntheses [12,18,19] fine grained quartz with particle size >230 mesh (FLUKA 83340) and course grained quartz sand with average particles around 40 mesh (Research Institute Kalk-Sand e.V., Hannover, Germany) were selected as silica sources. Lime was obtained by calcination of $CaCO_3$ (Johnson Mattay GmbH) at 1000 °C for 3 h. In all experiments this lime and the SiO_2 source were mixed according a CaO/SiO_2 ratio (*C*/*S*) of 0.5 as well as 0.8. Calcium-formate (Sigma 21134) was used in each experiment, yielding to a further increase of the total *C*/*S* ratio of each batch. The amount of this additive was adjusted according to a Ca-formate/lime ratio (*F*/*C*-ratio) of 0.5 and 0.25. The combination of the two *C*/*S* ratios and the two *F*/*C* ratios leads to a total number of four resulting *C*/*S* ratios: 0.67, 0.8, 1.0 and 1.24. The aim of investigation of this broad range was to test crystallization behavior in a composition interval around the ideal *C*/*S* of 0.83 of tobermorite [1–3] as well as to appreciate the effect of a high amount of Ca-formate too. The initial weights of the educts SiO_2, CaO and Ca-formate are summarized in Table 1. They were filled into 50 ml steel autoclaves with Teflon liners and 20 ml distilled water was added. The autoclaves were heated in an oven at 200 °C for 40.5 h. After this reaction time the pH-value of the solution was measured before the products were filtered, washed with water and dried at 80 °C for 24 h.

The synthesis products were analyzed by XRD, SEM/EDX and FTIR spectroscopy. X-ray powder data were collected on a Bruker Endeavor D4 powder diffractometer (Bragg-Brentano geometry) using Ni-filtered Cu Kα radiation at 40 kV and 40 mA. The measurements were performed with a step width of 0.03° in the range of 5–85° 2θ. 2668 steps of 1 s duration were measured. The data were analyzed using the WinXpow software of Stoe & Chi. The morphology and chemical composition of the synthesis products were analyzed on a Jeol JSM-6390A scanning electron microscope (SEM) at an accelerating voltage of 20 kV. The SEM was equipped with the EDX-analysis system JED 2003. The samples therefore were sputtered with a fine layer of gold to prevent electric charging during measurement. A signal of gold (Au) therefore exists in each EDX spectrum.

Infrared spectra were taken on a Bruker IFS66v FTIR spectrometer. The samples therefore were diluted by KBr (about 1 mg sample in 200 mg KBr), pressed into pellets and measured relatively to the KBr as a reference.

3. Results

3.1. XRD and SEM/EDX analysis of synthesis products

The results of qualitative phase analysis of the products according to X-ray powder diffraction are summarized in

Table 1
Experimental parameters and products of syntheses.

No.	CaO [g]	Ca-formate [g]	Ca-formate/CaO	*C*/*S*	SiO_2 source[a]	pH after synthesis	Phases according to XRD
1	0.75	0.43	0.25	0.67	P	7	quartz, tobermorite,
2	0.75	0.43	0.25	0.67	S	13	quartz, portlandite, tobermorite
3	1.16	0.67	0.25	1.0	P	9	quartz, disordered tobermorite,
4	1.16	0.67	0.25	1.0	S	12	portlandite, quartz, disordered tobermorite
5	0.75	0.85	0.5	0.8	P	7–8	quartz, disordered tobermorite/CSH-I
6	0.75	0.85	0.5	0.8	S	12	quartz, portlandite, disordered tobermorite/CSH-I
7	1.16	1.34	0.5	1.24	P	7	quartz, disordered tobermorite/CSH-I
8	1.16	1.34	0.5	1.24	S	12	quartz, portlandite, disordered tobermorite/CSH-I

[a] P: powdered quartz with particle size >230 mesh (FLUKA 83340), S: quartz sand with average particles around 40 mesh (Research Institute Kalk-Sand e.V., Hannover, Germany).