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FULL PAPER

Synthesis, structural characterization, and thermodynamic properties of 11Å Al-tobermorite

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Abstract

In the present paper, the structure as well as the solubility and thermodynamic data of synthesized Al-tobermorite is discussed. ^{29}Si NMR and XRD prove the successful synthesis of an Al-tobermorite with a ratio of Al/(Al + Si) = 0.1. The aluminum is incorporated in the branching (Q^3) sites of the silicate chains. Solubility of the synthesized Al-tobermorite can be calculated from the measured ionic concentrations from storage in aqueous solution, which show little variation over time. The tobermorite remains stable in aqueous solution. Consequently, an equilibrium between aqueous solution and the synthesized Al-tobermorite can be assumed. On the basis of the experiments, thermodynamic data for Al-tobermorite can be estimated and presented in the present paper.

KEYWORDS
aerated autoclaved concrete, Al-tobermorite, solubility, thermodynamic data

Abstrakt

In der vorliegenden Publikation werden die Löslichkeit undweitere thermodynamische Daten von synthetischem Al-Tobermorit diskutiert. ^{29}SINMR und XRD wurden verwendet um die erfolgreiche Synthese des Al-Tobermorit miteinem Verhältnis von Al/(Al + Si) = 0,1 nachzuweisen. Der Einbau des Aluminiumsfindet in den “Branching sites” (Q3) der Silikatketten statt. Die Löslichkeitwurde anhand der Ionenkonzentrationen aus der Lagerung des Al-Tobermorit inWasser bei verschiedenen Temperaturen bestimmt. Anhand der Ergebnisse kanngezeigt werden, dass der Einbau von Al die Löslichkeit der Tobermoriterniedrigt. Neue thermodynamische Daten werden präsentiert.

1 | INTRODUCTION

Besides other crystalline phases, tobermorite is one major phase of aerated autoclaved concrete [1–3]. Tobermorite is a calcium silicate hydrate phase. The main building block in the structure of tobermorite is the so called “dreierketten” silicate chain. It is known that certain amounts of aluminum can be incorporated into the structure of C-S-H phases [4, 5] as also observed for C-S-H in concrete or in crystalline

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tobermorite in aerated autoclaved concrete. This in turn results in so-called (alumina)silicate chains as a major structural unit in tobermorite and C-A-S-H phases.

The crystallochemical formula of tobermorite is $Ca_5[Si_6O_{17}]\cdot 5H_2O$, resulting in the formula of $Ca_5[H_{0.6}Si_{5.4}Al_{0.6}O_{17}]\cdot 5H_2O$ if silicon is replaced by aluminum by a ratio of Al/(Al + Si) = 0.1 [6].

Thermodynamic calculations became very important in the field of construction materials, inasmuch as the prediction of stable phase assemblages can be calculated from the chemistry of the raw materials used for the production of the building material. The predicted thermodynamically stable phase assemblage in turn is a key factor for understanding the performance (e.g., strength) and durability (e.g., resistance against chemical attack) of building materials [7, 8].

In the present publication the structure and thermodynamic data for $Ca_5[H_{0.6}Si_{5.4}Al_{0.6}O_{17}]\cdot 5H_2O$ (Al-tobermorite) is presented, for further details see also [9].

2 | MATERIALS AND METHODS

2.1 | Materials

In order to synthesize the Al-tobermorite SiO_2, $Ca(OH)_2$ and $Al(OH)_3$ and deionized water were mixed. The weight of the chemicals was done exactly for the composition of $Ca_5[H_{0.6}Si_{5.4}Al_{0.6}O_{17}]\cdot 5H_2O$ using a water solid ratio of 3 for the autoclavation process. After weighing and homogenization, the sample was autoclaved at 180°C for 20h (1.1 MPa steam pressure). Before characterization, the sample was dried at 60°C and smoothly ground.

2.2 | Methods

In order to characterize the synthesized Al-tobermorite several methods such as XRD, TGA, and NMR were used. XRD was performed using a D8 DaVinci diffractometer measuring from 5° to 75°. Starting point at 5° was chosen in order to measure the first basal reflex (001) at 7.5°. TGA was done using a TGA NETSCH STA 449 F1 Jupiter. Measurement was performed from room temperature to 1000°C with a heating rate 5°C/min. ^{29}Si NMR spectra were recorded using a Bruker Advance III NMR spectrometer equipped with a 7 mm CP/MAS probe applying 79.5 MHz. The sample rotation rate was 4500 Hz and 3072 scans were recorded. 30°-29Si-pulse of 2.5 us was used and 20 s relaxation delays. The RF field strength was 33.3 kHz during SPINAL64 proton decoupling

In order to calculate the solubility of the synthesized Al-tobermorite, the samples were re-equilibrated in aqueous solution at 3°C, 23°C, 40°C, and 60°C up to 120 days. Total concentrations for Al, Si, and Ca were measured using ICP-MS. The pH value was measured using a calibrated pH probe. From the total concentration the speciation and finally the solubility product K was calculated using thermodynamic modeling and following Equation (1).

$$K = \{Ca^{2+}\}^{0.833} \cdot \{HSiO_3{}^{-}\}^{0.9} \cdot \{AlO_2^{-}\}^{0.1} \cdot \{OH^{-}\}^{0.666} \cdot \left\{H_2O^0\right\}^{0.1} \quad (1)$$

TABLE 1 Thermodynamic data for Al-tobermorite according to the dissolution of Al-tobermorite following the equation $[Ca^{2+}]^{0.833} \cdot [HSiO_3{}^{-}]^{0.9} \cdot [AlO_2{}^{-}]^{0.1} \cdot [OH^{-}]^{0.6669} \cdot [H_2O^0]^{0.1}$. Adapted from Lothenbach et al. [9].

logK	$\Delta_f G^0$	$\Delta_f H^0$	S^0	C_p	Vol
	KJ/mol	kJ/mol	J/mol/K	J/mol/K	cm3/mol
−8.58	−1634.1	−1763	114	126	47.57

with {…} representing the respective chemical activities of the involved aqueous species in the precipitation reaction of Al-tobermorite. Activities were calculated using the extended Debye-Hückel equation.

The temperature dependency of the solubility product, K_T, of the synthesized Al-tobermorite was calculated following Equation (2).

$$\log KT = A0 + \frac{A2}{T} + A3\,lnT \quad (2)$$

where T is the temperature in K and A0, A2, A3 are empirical coefficients. If the entropy (S°), the enthalpy (Δ fH°), and the heat capacity are available, the coefficients A0, A2, A3 can be calculated directly [10].

The entropy (S°) and the heat capacity of Al-tobermorite were estimated from 11 Å-tobermorite, corundum(C), structural water (H), and quartz(Q) as discussed detailed in Lothenbach et al. [9].

Thermodynamic data for the synthesized Al-tobermorite is summarized in Table 1.

3 | RESULTS AND DISCUSSION

^{29}Si NMR results are shown in Figure 1. It can be seen that the Si sites identified in the synthesized Al-tobermorite correspond very well to a tobermorite structure with aluminum incorporation. Aluminum can be identified at Q^3 sites next to silica tetrahedra. Aluminum can replace silicon in a tetrahedral position at the Q^3 sites, whereby AlO_4-tetrahedra are not linked to each other. This in turn is in line with the Loewenstein rule.

Figure 2 shows the XRD patterns recorded for the synthesized Al-tobermorite and the Al-tobermorite after storage in aqueous solution for the determination of the solubility. It can be seen that the synthesis was successful and Al-tobermorite is present in the synthesized powder. The lattice parameter determined corresponds to a basal spacing of approximately 11.38 Å, which can be expected for an Al-tobermorite with a ratio of Al/(Al + Si) = 0.1 [9]. In addition, it shows that Al-tobermorite remains stable for up to 120 days of storage in aqueous solution. Consequently, it can be assumed that the calculated solubilities correspond to equilibrium conditions.

The concentration of the Si, Al, Ca in solution was measured at 30 days, 60 days, 90 days, and 120 days at different temperatures (3°C, 23°C, 40°C, and 60°C). The concentrations of each ion at 40°C storage is plotted against time in Figure 3 representative for all temperatures considered.

It can be seen that the total concentrations stay constant over time and an equilibrium between solution and tobermorite is achieved.

On the basis of the data shown in Figure 3 the solubility product of Al-tobermorite can be calculated according to Equation 1. The

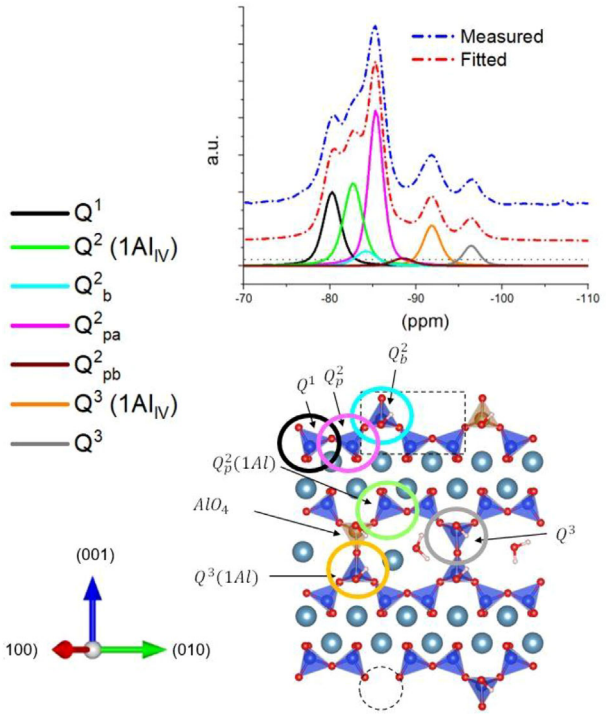

FIGURE 1 Top: ^{29}Si NMR spectrum of the Al-tobermorite synthesized; bottom: structure of Al-tobermorite with assignment of the Si sites identified by means of ^{29}Si NMR. Adapted from Lothenbach et al. [9].

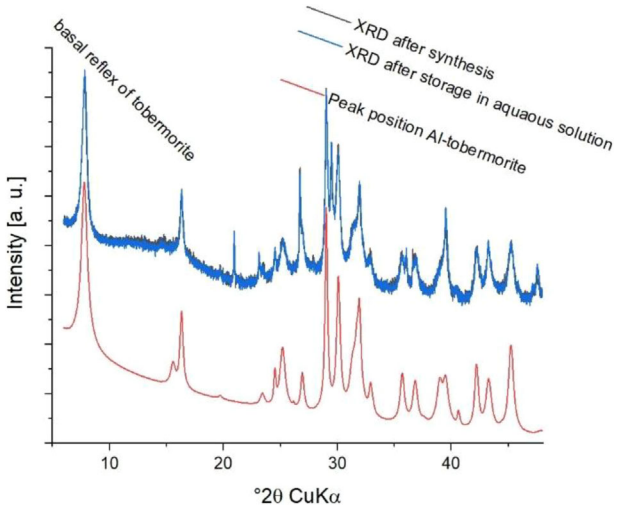

FIGURE 2 XRD patterns of the Al-tobermorite synthesized and the Al-tobermorite after storage in aqueous solution. Adapted from Lothenbach et al. [9].

solubility product was calculated for all temperatures chosen for the solubility experiments (at 3°C, 23°C, 40°C, and 60°C).

Additional to the measured solubilities, the temperature dependency of Al-tobermorite was calculated according to Equation 2 using the thermodynamic data shown in Table 1.

Figure 4 shows the solubility product (log K) plotted against temperature. The crosses show the solubility of the synthesized Al-

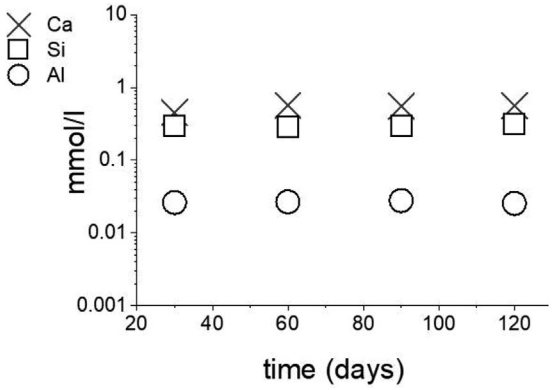

FIGURE 3 Ionic concentrations of Si, Al, Ca in the aqueous solution of the synthesized Al-tobermorite at 40°C storage. Adapted from Lothenbach et al. [9].

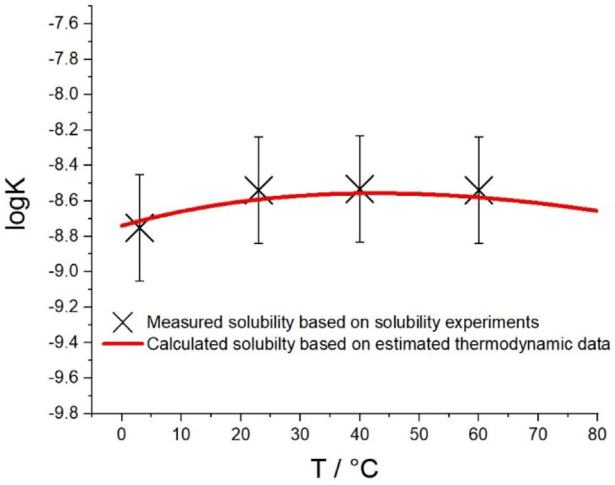

FIGURE 4 Solubility of Al-tobermorite based on solubility experiments and based on estimated entropy and heat capacity data. Adapted from Lothenbach et al. [9].

tobermorite calculated for different temperatures based on the data of the solubility experiments done. The red curve shows the calculated temperature dependency of the solubility of Al-tobermorite as calculated according to Equation 2 and the thermodynamic data shown in Table 1. It can be seen that there is a very good agreement between calculated and measured values.

This in turn leads us to the following conclusions:

1. Al-tobermorite was successfully synthesized.
2. The synthesized Al-tobermorite could be stored in aqueous solution and reached equilibrium after 120 days.
3. Based on the measured concentrations the solubility product for Al-tobermorite could be calculated.
4. The experimental solubility product shows the same temperature trends as the calculated solubility product based on estimated entropy and heat capacity data.
5. Consequently, the thermodynamic data shown in Table 1 can be recommended for Al-tobermorite.

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