



Stability in the system CaO–Al₂O₃–H₂O

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ABSTRACT

The solubility of AH₃, CAH₁₀, C₂AH_{7.5}, and C₃AH₆ was determined experimentally at 7 to 40 °C and up to 570 days. During the reaction of CA, at 20 °C and above initially C₂AH_{7.5} formed which was unstable in the long-term. The solubility products calculated indicate that the solubilities of CAH₁₀, C₂AH_{7.5} and C₄AH₁₉ increase with temperature while the solubility of C₃AH₆ decreases. Thus at temperatures above 20 °C, C₃AH₆ is stable, while at lower temperature also CAH₁₀ and C₄AH₁₉ are stable, depending on the C/A ratio.

At early hydration times, CAH₁₀ can be stable initially at 30 °C and above, as the formation of amorphous AH₃ stabilises CAH₁₀ with respect to C₃AH₆ + 2AH₃. With time, as the solubility AH₃ decreases due to the formation of microcrystalline AH₃, CAH₁₀ becomes unstable at 20 °C and above.

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1. Introduction

In order to understand and describe the hydration process of calcium aluminate cements, the CaO–Al₂O₃–H₂O system has been extensively studied under a wide range of temperatures (1 °C to 60 °C) [1–13]. Studies on the pure system showed that C₃AH₆¹ and CH are stable at ambient temperature, while CAH₁₀, C₂AH₈ (or rather C₂AH_{7.5}) and C₄AH_x are metastable (x = 13 or 19 depending on the relative humidity). Microcrystalline or amorphous AH₃ precipitates also; the more stable crystalline AH₃ (gibbsite) forms generally at higher temperatures only. The hydration of monocalcium aluminate (CA), the main constituent of the calcium aluminate cements, is strongly dependent on the temperature and on the reaction time. CAH₁₀ is the hydrate phase formed at temperatures below approximately 15 °C (CA + 10 H → CAH₁₀) [4,6,7,14]. Between approximately 15 and 30 °C, CAH₁₀, AH₃ together with C₂AH₈ (2CA + 11 H → C₂AH₈ + AH₃) is formed initially [13,15]. C₂AH₈ dehydrates to C₂AH_{7.5} within a few hours [15–17]. CAH₁₀ and C₂AH_{7.5} are metastable at 23 °C and above and convert with time to C₃AH₆ and to AH₃ according to the following reactions: 3CAH₁₀ → C₃AH₆ + 2AH₃ + 18H and 3C₂AH_{7.5} → 2C₃AH₆ + AH₃ + 7.5H.

A large number of studies has investigated the solubility of C₃AH₆ (hydrogarnet) within the temperature range from 1 °C to 250 °C [1–12], much less studies are available on the solubility of amorphous or microcrystalline AH₃ and of CAH₁₀ from 1 °C to 21 °C [4–8]. Despite the large number of studies on the solubility of C₃AH₆, the reported solubility products for C₃AH₆ vary over 3 log units [9,18,19]. This large variation has important implications on the calculated phase assemblage in hydrated cements. It has been shown that a difference of 1.2 log units is

sufficient to stabilise either monosulfate or hydrogarnet in hydrated Portland cements [20]. Thus, thermodynamic calculations predict apparently different stable hydrate assemblages. In addition, the formation of ettringite, CAH₁₀ and amorphous AH₃ has been predicted for calcium sulphoaluminate cements and in ternary formulations, while experimentally ettringite, monosulfate (C₄AsH₁₂) and AH₃ were observed [21–23]. This discrepancy indicates that the data compiled in the recent cement database cemdata2007 [9,24] for amorphous AH₃ and CAH₁₀ may not be reliable.

The current paper presents new experimental data for the system Al₂O₃–CaO–H₂O at 7, 20, 30 and 40 °C determined between 13 and 574 days of reaction. Based on the measured concentrations, solubility products for AH₃, CAH₁₀, C₂AH_{7.5} and C₃AH₆ were calculated and compared critically to other solubility measurements reported in literature. The newly derived thermodynamic data were used to visualise their relative stability as a function of temperature and time.

2. Methods

2.1. Sample preparation

To perform precipitation experiments at various C/A ratios, CA and CA₂ were synthesized from homogenized CaCO₃ and Al₂O₃ powder mixes (chemical grade). The powders were placed in two separate platinum crucibles and burnt for 1 h at 800 °C, 4 h at 1000 °C, and 8 h at 1400 °C (heating up 300 °C/h between each step), and subsequently cooled down inside the furnace at 600 °C/h. The resulting solids were ground and their Blaine surface area was measured to be 3790 cm²/g for CA and 6110 cm²/g for CA₂. The purity of the synthesized phases was checked by X-ray diffraction and Rietveld refinement analysis (with X'Pert HighScore Plus). Both samples contained 99% of the target composition. CA contained 99.1% CA and 0.9% C₁₂A₇; CA₂ was composed of 98.7 CA₂ and 1.3% CA.

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¹ Cement notation is used throughout the text: A: Al₂O₃, C: CaO, H: H₂O, c: CO₂, L: Li₂O.

All hydrated samples were prepared in a N₂-filled glove box, where the N₂ was bubbled through a KOH solution to minimize CO₂ contamination. For the precipitation experiments at various temperatures, about 2 g of CA was mixed with 50 ml of boiled MilliQ water. The formation of the hydrate phases was investigated in sealed PE-vessels at 7, 20, 30 and 40 °C. For each reaction time (13, 62, 182 and 574 days) a separate sample was prepared.

For the precipitation experiments at C/A ratios from 0.5 to 1.2, about 2 g of CA₂ and freshly prepared CaO, or CA and CaO were mixed with 50 ml of boiled deionized water and equilibrated at 20 °C.

The separation of the solid and liquid phases was done in the glove box under N₂-atmosphere by vacuum filtration through 0.45 μm nylon filters to eliminate colloidal particles. Nanometric particles, however, might pass the filter, although at the high pH of the solution, the presence of Al₁₃ or other Al-polymers is improbable. The solids were subsequently placed in a desiccator in the glove box and dried during 14 days over a saturated CaCl₂ solution prior to the analysis in order to equilibrate the samples with a relative humidity of about 30%.

2.2. Characterization of the solid phase

Samples were crushed and ground by hand to a particle size ≤ 63 μm under atmospheric conditions and immediately analysed by X-ray diffraction (XRD) and thermogravimetry (TGA/DTG). The XRD experiments were performed with a PANalytical X'Pert Pro MPD diffractometer in a θ–θ-configuration employing CuKα radiation. The powdered samples were scanned between 5° and 80° with the X'Celerator detector. The TGA analyses were performed with a Mettler Toledo TGA/SDTA851e, where ~10 mg of sample was placed in an open vessel under N₂ atmosphere, and investigated at a heating rate of 20 °C/min up to 980 °C.

2.3. Characterization of the liquid phase

Directly after filtration 4 ml of the liquid phase of each sample was collected and placed into two separate PE-vessels. In the first vessel 1 ml of solution was diluted (1:10) with HNO₃ (supra-pure, 6.5%) to avoid adsorption of dissolved ions by the PE-vessels and the precipitation of solids. The second vessel was filled with 3 ml of solution to determine the pH-value (immediately measured to avoid CO₂ contamination). A Knick pH-metre 766 and a Knick SE pH/Pt1000 electrode were used. In order to minimize the alkali error, fresh KOH solutions with known concentrations were measured (0.001 mol/l to 1 mol/l). The obtained values were correlated to the calculated H⁺ concentrations, considering the temperature during measurement (~23 °C) and the ionic strength of the KOH solutions. The total concentrations of the Ca and Al were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian VISTA Pro). The detection limit was 0.001 mmol/l for Ca and 0.004 mmol/l for Al. Calcium was measured at 0.003 mmol/l and Al at 0.005 mmol/l in the blank solution (HNO₃ 0.01 mol/l).

2.4. Calculation of thermodynamic data

The measured concentrations were used to calculate the solubility products of AH₃, CAH₁₀, C₂AH_{7.5} and C₃AH₆ between 7 °C and 40 °C:

$$\text{Al(OH)}_3 : K_{s0}(\text{1/2 AH}_3) = \{\text{Al(OH)}_4^-\} / \{\text{OH}^-\} \quad (1)$$

$$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O} : K_{s0}(\text{CAH}_{10}) = \{\text{Ca}^{2+}\} \cdot \{\text{Al(OH)}_4^-\}^2 \cdot \{\text{H}_2\text{O}\}^6 \quad (2)$$

$$\begin{aligned} 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 7.5\text{H}_2\text{O} : K_{s0}(\text{C}_2\text{AH}_{7.5}) \\ = \{\text{Ca}^{2+}\}^2 \cdot \{\text{Al(OH)}_4^-\}^2 \cdot \{\text{OH}^-\}^2 \cdot \{\text{H}_2\text{O}\}^{2.5} \end{aligned} \quad (3)$$

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} : K_{s0}(\text{C}_3\text{AH}_6) = \{\text{Ca}^{2+}\}^3 \cdot \{\text{Al(OH)}_4^-\}^2 \cdot \{\text{OH}^-\}^4 \quad (4)$$

$$\begin{aligned} 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O} : K_{s0}(\text{C}_4\text{AH}_{19}) \\ = \{\text{Ca}^{2+}\}^4 \cdot \{\text{Al(OH)}_4^-\}^2 \cdot \{\text{OH}^-\}^6 \cdot \{\text{H}_2\text{O}\}^{12} \end{aligned} \quad (5)$$

$$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O} : K_{s0}(\text{C}_4\text{AH}_{13}) = K_{s0}(\text{C}_4\text{AH}_{19}) / \{\text{H}_2\text{O}\}^6 \quad (6)$$

where {} denotes the activity of the dissolved species.

The activities of the different species were calculated from the measured total concentrations at the respective temperatures using the geochemical modelling code GEMS [25,26]. Chemical interactions involving solids, solid solutions, gas mixture and aqueous electrolyte are considered simultaneously. The default database of the GEMS code was used, which is based on the PSI chemical thermodynamic database [27] merged with the slop98.dat database for temperature and pressure corrections [28]. The activity coefficients of aqueous species y_i were computed with the built-in expanded extended Debye–Hückel equation in Truesdell–Jones form with individual parameters a_i (dependent on ion size) and common third parameter b_y :

$$\log \lambda_i = \frac{-A_y z_i^2 \sqrt{I}}{1 + B_y a_i \sqrt{I}} + b_y I \quad (7)$$

where z_i denotes the charge of species i , I the effective molal ionic strength, b_y is a semi-empirical parameter (~0.064 at 25 °C), and A_y and B_y are P,T-dependent coefficients. This activity correction is thought to be applicable up to approx. 1 M ionic strength [26].

The dependence of the solubility products from temperature can be expressed as:

$$\log K_T = A_0 + A_1 T + \frac{A_2}{T} + A_3 \ln T + \frac{A_4}{T^2} + A_5 T^2 + A_6 \sqrt{T} \quad (8)$$

[29,30], where A_0, \dots, A_6 are constants. If the entropy (S°), the enthalpy ($\Delta_f H^\circ$) as well all the coefficients (a_0, a_1, \dots) of the heat capacity equation ($C_p^\circ = a_0 + a_1 T + a_2 T^{-2} + a_3 T^{-0.5} + a_4 T^2$) of the species are available, the constants A_0, \dots, A_6 can be calculated directly (see [29,30]), otherwise the constants can be fitted to experimental data. If the heat capacity of the reaction, $\Delta_r C_p^\circ$, is assumed to be constant in the considered temperature range, Eq. (8) can be simplified to the so-called 3-term approximation:

$$\log K_T = A_0 + \frac{A_2}{T} + A_3 \ln T \quad (9)$$

$$A_0 = \frac{0.4343}{R} \cdot [\Delta_r S_{T_0}^\circ - \Delta_r C_{p,T_0}^\circ (1 + \ln T_0)] \quad (10)$$

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta_r H_{T_0}^\circ - \Delta_r C_{p,T_0}^\circ T_0) \quad (11)$$

$$A_3 = \frac{0.4343}{R} \cdot \Delta_r C_{p,T_0}^\circ \quad (12)$$

where T_0 is the reference temperature (298.15 K) and S° the entropy. The difference between the 7-term method in Eq. (8) and the 3-term approximation (Eq. (9)) is small over the temperature interval 0–100 °C [9,20]. A more detailed description of the temperature corrections used in GEMS is given elsewhere [29–31] and in the online documentation of GEMS. The entropy S° was adjusted to obtain the best fit between the measured solubility data at different temperatures and the calculated solubility products.

The heat capacity C_p° of hydrogarnet has been measured experimentally [32], while for CAH₁₀, C₂AH_{7.5}, and C₄AH_x no measured data are available. The value of the heat capacity of the reaction, $\Delta_r C_p^\circ$, has little influence on the calculated log K value in Eq. (8) in the temperature range 0–100 °C (see e.g. [20]) and is thus not fitted based on the measured solubility at different temperatures. The heat capacities of CAH₁₀, C₂AH_{7.5} and C₄AH_x were calculated based on a reference reaction

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