THERMODYNAMIC MODELLING OF THE EFFECT OF TEMPERATURE ON THE HYDRATION OF PORTLAND CEMENT

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Abstract

The composition of the phase assemblage and the pore solution of Portland cements hydrated between 0 and 60 °C can be modelled as a function of time and temperature. The results of thermodynamic modelling show a good agreement with experimental data. At 5 and at 20 °C, a similar phase assemblage was calculated to be present, while just below 50 °C, thermodynamic calculations predict the conversion of ettringite and monocarbonate to monosulfate. Modelling showed that in Portland cements, which have an SO₃/Al(Fe)₂O₃ ratio of < 1 (molar ratio), above 50 °C monosulfate and monocarbonate are present. In Portland cements which contain more SO₃ or less Al (SO₃/Al(Fe)₂O₃ > 1), at 50 °C and above monosulfate and ettringite are expected to persist.

1. INTRODUCTION

The hydration of cement is sensitive to temperature. Increased temperature promotes the hydration leading to high early strength. The 28 and 91 day strengths of mortars and concrete however, are found to be reduced at higher temperatures compared to samples hydrated at 20 or 5 °C, although the observed degrees of hydration are similar. In the case of increased temperature, the initially fast hydration causes the more rapid precipitation of hydration products during the first hours and days, which is responsible for the observed early strength development. This fast hydration in the initial stage leads to a more heterogeneous distribution of the hydration products as the hydrates precipitate around the clinker particles and build up a dense inner shell around the clinkers [1]. At low temperature, hydration starts very slowly, which allows the dissolved ions more time for diffusion before the hydrates precipitate and leads to a less dense C-S-H, a more even distribution of hydration products and less coarse porosity [1-3]. Different curing temperatures do not only change the morphology of the solid phases but influence also the phase assemblage: at 50 °C and above monosulfate is formed at the expenses of ettringite and monocarbonate [4]. The temperature also influences the composition of the pore solution. While the concentration of most ions changes little, sulfate concentrations increase strongly with temperature [4, 5].
Thermodynamic modelling can be used to calculate the influence of temperature on the hydrate assemblage [6]. In this paper, thermodynamic modelling is used to assess the influence of temperature and composition of the type and volume of the hydrate assemblage.

2. MATERIALS AND METHODS

2.1 Experimental methods

Modelling results are compared to experimental results gained from a Portland cement, CEM I 52.5 N HTS. The chemical compositions of the solids were determined by X-ray fluorescence analysis (XRF) and the amount of CO$_2$ by TGA as given in Table 1. Cement pastes were prepared at w/c of 0.4, isothermally cured at 5, 20 and 50 °C, and the composition of the liquid and solid phase was analysed, for details see [4, 7].

Table 1: Composition of the cement used given in weight-%

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>SO$_3$</th>
<th>CO$_2$</th>
<th>CaO$_{free}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>22.3</td>
<td>2.7</td>
<td>1.9</td>
<td>65.7</td>
<td>0.85</td>
<td>0.22</td>
<td>0.13</td>
<td>2.2</td>
<td>1.6</td>
<td>0.45</td>
</tr>
</tbody>
</table>

2.2 Thermodynamic modelling

When cement is brought into contact with water, easily soluble solids such as gypsum or calcite react until equilibrium with the pore solution is reached. The clinker phases hydrate slowly releasing Ca, Si, Al, Fe and hydroxide into the solution, which then can precipitate as C-S-H, ettringite or as other hydrate phases. The hydration model used in this study is described in detail by Lothenbach et al. [6, 8] and accounts for all the reactions described above. The composition of the solid and liquid phase as a function of time and temperature is calculated based on (i) the composition of the cement as given in Table 1, (ii) the calculated degree of the dissolution of the clinkers using a set of empirical equations (see [8]) and (iii) thermodynamic calculations using the dataset given. The acceleration of the hydration reaction at high temperatures is taken into account using the Arrhenius equation. The rate at the temperature $T$ is then calculated by $R_{t,T} = R_{t,T_0} e^{-\frac{E_a}{RT} \left( \frac{1}{T} - \frac{1}{T_0} \right)}$, where $T$ corresponds to the temperature of interest in K, $T_0$ to 293 K (20 °C) and $R_{t,T_0}$ to the rate at time $t$ calculated at 20 °C (for details see Lothenbach et al. [6]).

Thermodynamic modelling was carried out using the Gibbs free energy minimization program GEMS [9]. GEMS is a broad-purpose geochemical modelling code which computes equilibrium phase assemblage and speciation in a complex chemical system from its total bulk elemental composition. Chemical interactions involving solids, solid solutions, and aqueous electrolytes are considered simultaneously. The speciation of the dissolved species as well as the kind and amount of solids precipitated are calculated.

The thermodynamic data for aqueous species as well as for many solids were taken from the PSI-GEMS thermodynamic database [10, 11]. Solubility products for cement minerals including ettringite, different AFm phases, hydrogarnet, C-S-H and hydrotalcite were taken from a recent compilation: cemdata07 [6]. For modelling the formation of ideal solid solution between Al- and Fe-containing analogues has been assumed [6]. Thus, the expressions ettringite, monocarbonate, monosulfate, hemicarbonate or hydrotalcite in this paper all refer to the solid solution between the Al- and Fe-containing analogues. To describe the
composition of C-S-H a model based on two concurrent solid solution between jennite 
(C_{1.7}SH_{2.1}) and tobermorite (C_{0.83}SH_{1.3}) and between tobermorite and SiO_2 was used [6, 12].

3. RESULTS AND DISCUSSION

3.1 Hydration at different temperatures

Increased temperatures initially accelerate the dissolution of the anhydrous clinker phases as illustrated in Figure 1. The initially faster hydration at higher temperatures results in the precipitation of significant amounts of hydration products during the first hours and days at elevated temperatures, which is also mirrored in a faster strength development, see e.g. [4, 13]. After longer hydration times, however, a similar degree of hydration is observed, while the compressive strength of samples hydrated at lower temperature is generally higher. In accordance with the measured data, the calculated progress of hydration at 50 °C is initially fast, but slows down, while at 5 °C the dissolution starts at a much slower rate but progresses more steadily so that the calculated degrees of hydration are similar after 150 days (Figure 1).

![Figure 1: Measured (dots) and calculated (lines) dissolution of alite in the cement paste as a function of temperature and time. Measured data taken from [6].](image)

Thermodynamic modelling was used to calculate the phase assemblage at different temperatures (Figure 2). In agreement with the experimental observations, thermodynamic modelling predicts at 5 and at 20 °C the same phase assemblage: C-S-H, portlandite, ettringite, monocarbonate as well as small quantities of calcite and hydrotalcite. At 50 °C, the presence of monosulfate is predicted but no or only very little ettringite. This agrees well with experimental data for this cement [4]: at 5 and 20 °C ettringite and monocarbonate have been found to be the main hydration products besides C-S-H and portlandite [4]. At 50 °C, initially, the formation of ettringite has been observed. After 150 days of hydration at 50 °C, however, clearly less ettringite than for samples hydrated at 20 °C and no monocarbonate was found but monosulfate [4]. Not only the kind, but also the quantities of hydrates (portlandite, ettringite) formed at the different temperatures and the amount of pore solution agreed well with experimental data (see [6, 7]).
Figure 2: Calculated hydration of Portland cement as a function of time at A) 5 °C, B) 20 °C and C) 50 °C.
3.2 Hydrates formed at different temperatures

Thermodynamic modelling can also be used to calculate the hydrate assemblage at any hydration time as a function of temperature. To facilitate comparison between the different temperatures it was assumed that all clinker has hydrated. Thermodynamic modelling predicts for the Portland cement investigated C-S-H, portlandite, monocarbonate and ettringite as the main hydration products in the temperature range 0-47 °C (see Figure 3). Above 48 °C ettringite and monocarbonate are predicted to be unstable with respect to monosulfate:

\[
\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} + 2[3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCO}_3\cdot11\text{H}_2\text{O}] \Leftrightarrow 3[3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O}] + 2\text{CaCO}_3 + 18\text{H}_2\text{O}.
\]

The observed changes in the composition around 47 °C agree well with experimental observations. At 50 °C a significant reduction of the amount of ettringite and monocarbonate compared to 20 °C and the presence of monosulfate has been observed [4]. Christensen et al. [14] observed for a white Portland cement the presence of ettringite below 48 °C. At 48 °C and higher, no ettringite was present but monosulfate, which agrees well with the calculations presented here. It should be noted, that the temperature at which monosulfate is more stable than ettringite (or monocarbonate) depends strongly on the pH values of the solution and on the SO$_3$/Al$_2$O$_3$ ratio in the systems (see below). Ettringite has been found to exist in diluted systems up to 75 °C and higher [15, 16].

The formation of monosulfate at the expenses of ettringite and monocarbonate results in a significant reduction of the volume of the hydrated cement, which could be, besides the increase of coarse porosity due to the formation of denser C-S-H, one of the main factors for

![Figure 3: Calculated volume of solids in a hydrated cement paste as a function of temperature.](image-url)
the observed lower compressive strength at higher temperatures. However, not only the hydrate assemblage is influenced by the temperature but also the morphology of the hydrates. At 5 °C, the presence of long ettringite needles is observed and the formation of a less dense but more voluminous inner C-S-H, resulting in a reduction of the coarse porosity [4, 17]. The reduction of the coarser porosity is expected to be an important factor for the increased compressive strength at lower temperatures.

3.3 Influence of the SO3/(Al,Fe)2O3 ratio on stable hydrate assemblage

Not only the temperature but also the composition of cement strongly influences the stable hydrate assemblage and thus the porosity. Besides the main oxides, the fraction of carbonate and sulfate present in a cement can play a very important role. The presence of small amounts (2-3 %) of limestone has been found to stabilise monocarbonate and indirectly also ettringite, resulting in a higher volume of the hydrated cement and thus in a somewhat reduced porosity compared to samples without limestone [8, 18]. Similarly, the amount of sulfate added has an important influence on the kind and amount of hydrates that form during hydration (Figure 4). The addition of SO3 regulates not only the setting but influences also the volume of the hydrated assemblage, the remaining porosity and thus indirectly also compressive strength and the tendency for expansion. At 20 °C, a relatively high addition of SO3 will lead after longer hydration times to higher amounts of ettringite and, theoretically, to less porosity but also to a higher probability of expansion. These theoretical calculations agree with experimental data [19], where an increase of compressive strength at later times is observed in samples containing more SO3.

For cements hydrated at 50 °C or higher, the effect of more SO3 addition is somewhat modified. Monosulfate is calculated to form at the expenses of monocarbonate at increasing SO3 contents. Thus, in the range of the SO3 content of commercial cements, no or only very little increase of the volume as a function of SO3 can be expected for cements hydrated at 50 °C or higher. Thus, the difference in the volume of hydrated cements induced by the hydration temperature will depend strongly on the SO3/(Al,Fe)2O3 of the cement and will be most pronounced at SO3/(Al,Fe)2O3 ~ 1 (see Figure 4). Above a SO3/(Al,Fe)2O3 ~ 1, ettringite instead of monocarbonate is modelled to persist beside monosulfate. The presence of significant amounts of Mg in the clinker will lower this ratio as the formation of hydrotalcite will consume Al and Fe. It should be noted that the calculations have been carried out assuming complete hydration. The ratio of available SO3/(Al,Fe)2O3 of a hydrating cement will always be higher than the total ratio in the unhydrated cement, as only a part of the Al (and Fe) present in the cement will have reacted.

4. CONCLUSIONS

The results of thermodynamic modelling of the hydration at 5, 20 and 50 °C show a good agreement with experimental data. At 5 and 20 °C a similar phase assemblage is present. Thermodynamic calculations predict that in the Portland cements up to approx. 47 °C ettringite and monocarbonate are stable, while at higher temperatures monosulfate becomes more stable, which agrees with experimental observations in Portland cement systems [4, 14]. The changes of the hydrates assemblage around 47 °C decrease the volume of solids formed in the hydrated cement. This reduction is, beside the changes in porosity induced by the denser inner C-S-H, most probably an important factor for the reduced compressive strength observed for mortar and concrete samples hydrated at higher temperatures.
Modelling showed that the SO$_3$/\((\text{Al,Fe})_2\text{O}_3\) ratio of the hydrated cement determines whether above 47 °C ettringite or monocarbonate will continue to exist beside monosulfate.

A comparison of calculated porosities of mortar samples with measured compressive strength and porosity data for different cements after a range of hydration times and temperatures showed a good correlation, indicating that the space filling as calculated by thermodynamic models correlates with experimentally observed properties.
REFERENCES


