Paste models for hydrating calcium sulfates, using the approach by Powers and Brownyard

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Abstract

In the present paper paste models are presented for pastes consisting of calcium sulfates anhydrite ($\text{CS}$) and hemihydrate ($\text{CSH}_0:5$) that hydrate to the hydration product dihydrate/gypsum ($\text{CSH}_2$). A similar approach is followed as used for hydrating cement by Powers and Brownyard [19]. Closed-form equations are derived for the volume fraction of the unreacted binder (the considered calcium sulfate), unreacted water, chemical shrinkage and hydration product (gypsum). The derived equations, governing the paste composition, depend on the composition of the binder and of the water-binder ratio, and of the degree of hydration. The equations are in good agreement with information from literature, empirical and theoretical.

1. Introduction

In the presence of water, the calcium sulfates anhydrite ($\text{CS}$) and hemihydrate ($\text{CSH}_0:5$) hydrate to the hydration product dihydrate/gypsum ($\text{CSH}_2$). In this paper paste models are presented for such systems, following the same Powers and Brownyard [19] approach as used for hydrating cement. They were the first to systematically investigate the reaction of Portland cement and water and the formation of cement paste. In the late 1940s, they presented a model for hydrated cement paste in which unreacted water and cement, the hydration product, and shrinkage were distinguished (Fig. 1). Major paste properties were determined by extensive and carefully executed experiments, including the amount of retained water and the chemical shrinkage associated with hydration reaction.

Czernin [8], Locher [15], Hansen [11], Taylor [23], Neville [16], Jensen and Hansen [12], Brouwers [3,4,5,6] and Livingston et al. [14] summarize the most important features of the model, the methodology of which will be applied here to the hydration of calcium sulfates. Here, the subscript ‘c’ thus stands for either $\text{CS}$ or $\text{CSH}_0:5$, and hydration product stands for $\text{CSH}_2$, see Fig. 1, and expressions for the four volume fractions are derived. In contrast to the hydration of cement, upon the hydration of calcium sulfates there is one hydration product only, viz. gypsum, of which the density and molar mass are well known. Here, attention is restricted to anhydrite, hemihydrate and gypsum, but with varying temperature and/or partial water vapor pressure also so-called subhydrates can be formed, such as $\text{CSH}_x(0.5 \leq x \leq 0.8)$ [7,13,1,17]. Physically absorbed water to gypsum is not considered either, which may amount a few percent by mass at room temperature and moderate relative humidities [29].

2. Paste model

The hydration product contains the water that is (chemically and physically) combined with the calcium sulfate, named $w_h$, which is expressed in mass of water per reacted mass of calcium sulfate, so $w_h/c$. Consequently, it also follows that the volume...
and mass of the hydrated calcium sulfate, i.e. the hydration product (gypsum), reads

\[ V_{hp} = CV_c + W_dV_d; \quad m_{hp} = c + W_d, \]  

in which \( v_c \) is the specific density of the considered calcium sulfate. Note that the volume change involved with the hydration reaction is accounted for by assigning a specific volume, \( V_d \), to the water reacted. The specific volume of the gypsum now follows from

\[ V_{hp} = \frac{V_{hp}}{m_{hp}} = \frac{CV_c + W_dV_d}{c + W_d} = \frac{v_c + W_dV_d/c}{1 + W_d/c}, \]  

see Eq. (1). In contrast to \( v_d \), \( v_{hp} \) is known; hence the specific volume of the combined water follows by rewriting Eq. (2) as

\[ v_d = \frac{v_{hp} - (1 + W_d/c)}{W_d/c}. \]  

The volume fractions in the paste, see Fig. 1, follows [3] as:

\[ \varphi_{hp} = \frac{m}{V_w} \left[ \frac{v_c + W_dV_d}{V_w} - \frac{V_w}{V_w + c} \right], \]  

\[ \varphi_c = \frac{(1 - m)}{V_w} \left[ \frac{V_w}{V_w + c} - \frac{V_w}{v_c} \right], \]  

\[ \varphi_w = \frac{W_0 - m}{V_w} \left[ \frac{W_d}{c} - \frac{V_w}{V_w + c} \right], \]  

\[ \varphi_s = \frac{W_0 - m}{V_w} \left[ \frac{W_dV_d}{c} - \frac{V_w}{V_w + c} \right], \]  

in which \( v_w \) is the specific volume of free (uncombined) water. It readily follows that \( \varphi_c + \varphi_{hp} + \varphi_w + \varphi_s = 1 \), so the total paste volume (Fig. 1) is completely comprised by these four fractions. In Eqs. (4)–(7), \( W_0/c_0 \) is the water-calcium sulfate ratio (mass based) and \( m \) the maturity or the degree of reaction, i.e. \( c/c_0 \). The total capillary void fraction \( \varphi_{cp} \) amounts to \( \varphi_w + \varphi_s \) and follows from adding Eqs. (6) and (7) to

\[ \varphi_{cp} = \frac{W_0 - m}{V_w} \left[ \frac{W_dV_d}{c} - \frac{V_w}{V_w + c} \right], \]  

which constitutes the total void fraction of the paste.

The maturity \( m \) can take a value between zero (fresh mix, Fig. 1a) and at most unity. The maximum maturity depends on the amount of water in the system. The total water in the system is governed by [3]

\[ W_t = \frac{W_0}{c_0} + m \left( \frac{W_d}{c} \right), \]  

From this equation one can see that the total mass of the paste increases with increasing degree of hydration when external water may enter the paste to occupy the volume created by chemical shrinkage. The imbibed water is accounted for by the second term on the right-hand side of Eq. (9). The maximum achievable maturity follows as:

\[ m \leq \frac{W_0}{W_d/c}. \]  

Using Eqs. (9) and (10), the maximum maturity follows from

\[ m \leq \frac{W_0}{W_d/c} \quad \text{and} \quad m \leq \frac{W_0}{W_dV_d/c}, \]  

for sealed and saturated hydration, respectively. When the right hand-sides in Eqs. (10) and (11) exceed unity, then the maximum \( m = 1 \).

From Eq. (11) and when \( V_d < v_{hp} \), it follows that the amount of initial water can be smaller than the water needed for complete hydration, \( W_d \), owing to the inflow of external water by shrinkage. Physically this implies that to achieve complete hydration (\( m = 1 \)), upon mixing less water is required than \( W_d/c \), as the paste will imbibe the missing water (vapor) by the internal volume that is created by shrinkage.

3. Application to calcium sulfates

The reaction of anhydrite and water reads

\[ \text{CaSO}_4 + 2H_2O \rightarrow \text{Ca} (OH)_2, \]  

(12)

and the reaction of hemihydrate and water reads

\[ \text{CaSO}_4 \cdot 1.5H_2O \rightarrow \text{Ca} (OH)_2 \]  

(13)

The mass of combined water on mass of reacted calcium sulfate, \( w_d/c \), follows from Eqs. (12) and (13) and the molar masses of \( \text{CS} \) and \( \text{CSH}_{1.5} \), respectively, on the one hand, and the amount of involved \( H \) in reactions (12) and (13) and its molar mass on the other table

<table>
<thead>
<tr>
<th>Substance</th>
<th>( M ) (g/mole)</th>
<th>( \rho ) (g/cm³)</th>
<th>( \gamma ) (cm³/g)</th>
<th>( \omega ) (cm³/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CS} )</td>
<td>136.14</td>
<td>2.580</td>
<td>0.388</td>
<td>52.77</td>
</tr>
<tr>
<td>( \text{CSH}_{1.5} )</td>
<td>145.15</td>
<td>2.757</td>
<td>0.363</td>
<td>52.64</td>
</tr>
<tr>
<td>( \text{CSH}_2 )</td>
<td>145.15</td>
<td>2.628</td>
<td>0.381</td>
<td>55.23</td>
</tr>
<tr>
<td>( \text{C} )</td>
<td>172.17</td>
<td>2.310</td>
<td>0.433</td>
<td>74.53</td>
</tr>
<tr>
<td>H</td>
<td>100.09</td>
<td>2.711</td>
<td>0.369</td>
<td>36.92</td>
</tr>
</tbody>
</table>

Fig. 1. Breakdown of the calcium sulfate paste model (\( m = 0 \) and \( m > 0 \)), where \( V_w \) = unreacted water volume, \( V_c \) = unreacted anhydrite/hemihydrate volume, \( V_s \) = shrinkage volume and \( V_{hp} \) = dihydrate (gypsum) volume.
Table 2

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \nu_m / \nu_w )</th>
<th>( \nu_w / \nu_m )</th>
<th>( \nu_m / \nu_w )</th>
<th>( \nu_w / \nu_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CS}_7(\alpha) )</td>
<td>0.39</td>
<td>0.265</td>
<td>0.60</td>
<td>0.160</td>
</tr>
<tr>
<td>( \beta\text{SH}_5(\alpha) )</td>
<td>0.36</td>
<td>0.186</td>
<td>0.81</td>
<td>0.151</td>
</tr>
<tr>
<td>( \beta\text{SH}_5(\beta) )</td>
<td>0.38</td>
<td>0.186</td>
<td>0.71</td>
<td>0.133</td>
</tr>
</tbody>
</table>

(Table 1), the resulting \( w_d/c \) for the three considered reactions are included in Table 2. Moreover, for anhydrate, \( \alpha \)-hemihydrate and \( \beta \)-hemihydrate, \( \nu_w/\nu_m \) is 0.39 cm\(^3\)/g, 0.36 cm\(^3\)/g and 0.38 cm\(^3\)/g, respectively. These specific volumes readily follow by taking the reciprocal of the specific densities (Table 1), and the resulting \( \nu_m/\nu_w \) is included in Table 2 (based on \( \nu_m = 1 \) cm\(^3\)/g). The specific volume of the reacted water can now readily be computed by using Eq. (3), the result is included in Table 2 as well.

The compressed water volume can also be obtained in an alternative way. Deducing the molar volume of \( \text{CS}_7 \) from that of \( \text{CSH}_3 \) (Table 1) yields 21.76 cm\(^3\)/mole. This volume corresponds to the volume of the involved water, 2 mol of H per mole of \( \text{CS}_7 \), so that the molar volume of the compressed water \( \omega_m = 10.88 \text{ cm}^3/\text{mole} \). Using \( M_w = 18.02 \text{ g/mole} \) and \( \nu_m = 1 \text{ cm}^3/\text{mole} \), it also follows that \( \nu_{vd}/\nu_m = 0.60 \) (Table 2). For the hemihydrates, deducing their molar volumes from that of \( \text{CSH}_3 \) (Table 1), yields 21.89 cm\(^3\)/mole and 19.30 cm\(^3\)/mole for \( \alpha \)-\( \text{CSH}_5 \) and \( \beta \)-\( \text{CSH}_5 \), respectively. These volumes correspond to the volume of the involved water, 1.5 mol of H per mole of reacted \( \text{CSH}_5 \). This implies that the specific molar volumes of the compressed water, \( \omega_a = \omega_w = 15.49 \text{ cm}^3/\text{mole} \) and 12.87 cm\(^3\)/mole, for \( \alpha \)-\( \text{CSH}_5 \) and \( \beta \)-\( \text{CSH}_5 \), respectively. Using \( M_w = 18.02 \text{ g/mole} \) and \( \nu_m = 1 \text{ cm}^3/\text{mole} \), it again follows that \( \nu_{vd}/\nu_m \) amounts to 0.81 and 0.71 (Table 2).

In Eqs. (4)–(8), \( w_d/c \) is the water-binder ratio and \( \nu_m/\nu_w \) the specific volume of binder divided by that of free water. Eqs. (4)–(8), with the parameters given in Table 2, govern the volume fractions in the paste at a given maturity (reaction degree) \( m \). In Table 2 also the mass of water that can imbibe upon hydration is included, computed using Eq. (9). One can see that, potentially, more than 10 g of water can imbibe when 100 g of anhydrate reacts or in other words, 10 ml of internal volume is created in the paste (using \( \nu_m = 1 \text{ cm}^3/\text{g} \)). For the hemihydrates this figure amounts 3.5 to 5.4 ml per 100 g of reacted material.

Eq. (11) limits the maximum maturity, which depends on the amount of water in the system, whereby \( m \) is maximized by unity. In practice, due to workability requirements, sufficient water is present to accomplish full hydration, which is also achieved relatively fast. In case of full hydration, \( m = 1 \), the paste consists of hydration product/gypsum (Eq. (4)) and capillary space/voids (Eq. (8)) only. Presuming \( m = 1 \), Schiller [21] also derived Eq. (8) as porosity of hydrated gypsum, "Eq. (17); in which the employed values correspond to the values for \( \beta \)-\( \text{CSH}_5 \) that are listed in Table 2. The validity of this equation was confirmed by Soroka and Sereda [22] and Phani et al. [18]. By De Korte and Brouwers [10], Eqs. (4)–(7) were fruitfully used to analyze ultrasound speed analysis measurements of hydrated (0 ≤ \( m \) ≤ 1) \( \beta \)-\( \text{CSH}_5 \) paste.

4. The presence of inert minerals

The calcium sulfate binder may also contain a non-reactive mineral. Hemihydrates can for instance be produced by a flue gas desulphurization (FGD) installation. Consequently, the hydrated product is called FGD gypsum. This hemihydrate binder will contain remnants of limestone, which may take up to 30% (\( x_{\text{L}} \)) in the binder. In such case the actual chemically bound water will then read

\[
w_d/c = 0.186 x_{\text{CSH}_5}.
\]

whereby \( x_{\text{CSH}_5} \) is the hemihydrate mass content of the binder and the coefficient is taken from Table 2, and hence, it also follows that

\[
w_d/\nu_w = 0.133 x_{\text{CSH}_5}.
\]

for \( \beta \)-\( \text{CSH}_5 \) (Table 2). The specific volume of the binder follows from

\[
\nu_c = x_{\text{CSH}_5} \nu_c^{\beta\text{CSH}_5} + x_{\text{L}} \nu_c^{\text{L}}.
\]

Using Eq. (2) to eliminate \( \nu_c/\nu_w \) from Eq. (7), the shrinkage volume fraction can be written as

\[
\phi_p = \frac{m}{\nu_c} \frac{\nu_c}{\nu_w} \frac{1 + \nu_w}{\nu_w} \frac{\nu_c}{\nu_w}.
\]

This equation corresponds with ‘Eq. (3)’, proposed for \( \beta \)-\( \text{CSH}_5 \) by Sattler and Brückner [20] when \( m = 1 \) (fully hydrated system) is considered, and invoking \( \nu_w/\nu_{hp} = 2.31 \) (Table 1) and \( \nu_w/\nu_c \) = 2.63 and \( w_d/c = 0.186 \) (Table 2). For a fully hydrated system (\( m = 1 \)) consisting of \( \beta \)-hemihydrate only (\( x_{\text{CSH}_5} = 1 \), Eqs. (7) and (17) are compatible and both yield a nominator of about 5.3%.

But Sattler and Brückner [20] erroneously also proposed to use Eq. (17), with unaltered \( w_d/c \) and \( \nu_c/\nu_w \) for binders whereby \( x_{\text{CSH}_5} < 1 \). They correctly used Eq. (14) to compute the \( w_d/c \), but ignored the effect of this lower \( w_d/c \) on \( \nu_w/\nu_{hp} \), see Eqs. (2) and (15). When \( x_{\text{CSH}_5} < 1 \), \( \nu_w/\nu_{hp} \) cannot anymore be taken to be 2.31, as the hydration product is not consisting solely of gypsum, but also of limestone. For \( x_{\text{CSH}_5} = 0.91 \) and a fully hydrated system, following Sattler and Brückner [20] the nominator then yields 4.4%, whereas Eq. (7) (or Eq. (17)) with correctly computed \( \nu_{hp}/\nu_w \), i.e. by using Eq. (2)) has a nominator of 4.9%. The deviation between the two computations will even be more pronounced when the limestone content is further increased, e.g. to \( x_{\text{L}} = 0.3 \) and hence \( x_{\text{CSH}_5} = 0.7 \). In that case, the procedure by Sattler and Brückner [20] applied to Eq. (17) yields a nominator of 2.1%, whereas the correct computation yields 3.8%.

It is noteworthy that in the above computation \( \nu_c \) is taken to have the value of \( \beta \)-\( \text{CSH}_5 \). Actually, it has to be computed using Eq. (16). Using the reciprocals of the specific densities of gypsum and limestone (Table 1), Eq. (16) yields the specific volume of the binder.

![Fig. 2. Porosity (\( \phi_{cp} \)) of gypsum versus initial water-binder ratio (\( w_d/c_0 \)) for fully hydrated binder consisting of pure \( \beta \)-\( \text{CSH}_5 \), and a blend of \( \beta \)-\( \text{CSH}_5 \) (95% m/m) and limestone (5%), employing Eq. (8) and as measured.](image-url)
binder being $\rho_s = 2.652 \text{ g/cm}^3$ (or $\nu_s = 0.38 \text{ cm}^3/\text{g}$) for $x_C = 0.3$ and hence $x_{\text{Limestone}} = 0.7$. One can see that, even for this large content of limestone, $\rho_s$ is close to the value of plain $\rho_{\text{plain}}$, as the densities of limestone and $\beta$-hemihydrate are similar (Table 1).

5. Comparison with experiments

Yu and Brouwers [25] produced 40 mm $\times$ 40 mm $\times$ 160 mm specimens using a binder consisting of 95% ($x_{\text{C,SH}_0}$) $\beta$-C$_3$S-H$_2$O and 5% ($x_C$) limestone, with different water-binder ratios ($w_0/c_0$), namely 0.65, 0.8, 0.95 and 1.1. The mixes were prepared according to DIN EN 13279-2: after mixing they were stored for 7 days at room temperature, then dried at 40 °C to constant mass, and subsequently the mass and sizes were measured, resulting in the apparent density. Due to high water-binder ratio (compared to the stoichiometric value for complete hydration: 0.177, see Eq. (14)) and long hardening time, full hydration ($m = 1$) can be assumed, hence $\psi_c$ (the volume fraction of unreacted hemihydrate) is zero, see Eq. (5). And by the drying procedure, possible absorbed water will be removed, so that one can expect the samples only to consist of hydration product (pure gypsum and limestone) and porosity. Comparing the specific (gypsum) density (Table 1) with the measured apparent density yields the total porosity ($\psi_{\text{cp}}$).

In Fig. 2 the measured porosity is plotted versus $w_0/c_0$ as well as the computed values. The porosity is computed using Eq. (8) employing the $\beta$-C$_3$S-H$_2$O values listed in Table 2. One computation is based on $w_0/c_0 = 0.186$, applicable to pure hemihydrates, and the other on $w_0/c_0 = 0.177$ (Eq. (14) with 95% hemihydrate content). One can see that both computed values agree very well with the measured void fraction, and that the microstructural model that accounts for the true composition of the binder performs best, confirming the validity of the current calcium sulfate paste model. Obviously, with larger limestone contents the deviation with the plain $\beta$-C$_3$S-H$_2$O model will become even more pronounced.

6. Conclusion

In the present paper a paste model is derived for hydrating calcium sulfates, viz. for anhydrite, $\alpha$-hemihydrate and $\beta$-hemihydrate, which react to dihydrate (gypsum). Using a similar approach as for the cement paste model of Powers and Brownyard [19], equations are derived for the volume fraction of the unreacted binder (the considered calcium sulfate), unreacted water, chemical shrinkage and hydration product (gypsum). To this end, the specific volume of the “compressed water” of each hydration reaction is derived ($\psi_{\text{cp}}$).

The derived equations governing the paste composition (Eqs. (4)–(7), Table 2) depend on the degree of hydration ($m.0 < m < 1$) and the composition of the mix, governed by $w_0/c_0$, i.e. the water-binder ratio (mass based). Also the effect of possible inert minerals in the binder, i.e. limestone, can in a straightforward manner be accounted for in the model. The present equations are compared with available information from literature, theoretical and empirical, and found to be in good accord with them.

References