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Citation for published version (APA):

Document status and date:
Published: 01/01/2011

Document Version:
Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Download date: 28. Mar. 2019
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Ultrasonic sound speed of hydrating calcium sulphate hemihydrate; part 2, the correlation of sound velocity to hydration degree

Abstract
In this article the sound velocity through a mix is correlated to the hydration degree of the mix. Models are presented predicting the sound velocity through fresh slurries and hardened products. These two states correspond to the starting and finishing point of the hydration process. The present research shows that a linear relation between the amount of hydration-product (gypsum) formed (Smith et al., 2002) and sound velocity can be used to describe this process. To this end, the amount of hydration-product formed is determined by the using the equations of Schiller (1974) for the hydration process and of Brouwers (2010) for the volume fractions of binder, water and hydration products during the hydration process. The presented model shows that the induction time and gypsum growth rate are linear related to the water/gypsum ratio.

Introduction
In part 1, the ultrasonic speed measurements were compared with theoretical predictions for both the fresh slurry and the fully hydrated material. Based on these results we are now able to predict two points during the hydration process, namely the starting and completion of the hydration. Currently, the process in between these two stages has not been described yet. This article addresses the hardening stage as well as a model to relate the hydration degree to time.

Relation between hydration degree and sound velocity
Smith et al. /1/ describe the relation between hydration mechanism and ultrasonic measurements in aluminous cement. They provide a correlation between hydration degree and ultrasonic measurements. This correlation reads

\[ \alpha = \frac{c_e - c_{sl}}{c_{hp} - c_{sl}} + \alpha_0 \]

(1)

With \( c_e \) is the measured sound velocity through mix, \( c_{sl} \) is the sound velocity at moment the velocity starts increasing (so, of the slurry), \( c_{hp} \) is the sound velocity when the velocity stops increasing (so, of the hardened product) and \( \alpha_0 \) is the hydration degree at moment of \( c_{sl} \) (which is here zero).

The sound velocity of slurry and hardened product were presented in Part 1. The sound velocity of the slurry appeared to be best represented by Robeyst et al. /2/, which reads;
\[
\frac{1}{c_{sl}^2} = \left(1 - \frac{c_{air}}{\phi_t} \right) + \frac{c_{air} \phi_t}{K_w \phi_t K_{air} + K_{III}} \left(1 - \frac{\phi_t}{\phi_i} \right).
\]

\[
\left( \rho_f \left( \frac{\phi_t}{\phi_i} + \frac{(1 - \phi_t)}{2} \left(1 + 2(1 - \phi_t) \right) \right) \right) + \frac{1}{2} \rho_f \left(1 + 2(1 - \phi_t) \right)
\]

\[
\frac{1}{c_{sl}^2} = \left(1 - \frac{c_{air}}{\phi_t} \right) + \frac{c_{air} \phi_t}{K_w \phi_t K_{air} + K_{III}} \left(1 - \frac{\phi_t}{\phi_i} \right).
\]

The sound velocity of the hardened product was best described by Ye /3/, reading

\[
c_{hp} = \frac{c_{DH} c_{f}}{1 - \phi_t c_f + \phi_t c_{DH}}
\]

Finally, Eq. (1) can be rewritten to

\[
c_e = \alpha (c_{hp} - c_{sl}) + c_{sl}
\]

when it is invoked that \( \alpha = 0 \) corresponds to \( c_e = c_{sl} \) and \( \alpha = 1 \) corresponds to \( c_e = c_{hp} \).

**Analytical hydration models**

In this section, analytical hydration models are described which relate the hydration degree and time. In literature several different hydration models are introduced. Most models are based on the work of either Schiller /4-7/ or Ridge and Surkevicius /8-10/.

The equation of Schiller /4/ has the advantage that it indirectly includes the water/binder ratio in the parameters. The equation of Schiller /4/ reads

\[
t = K_1 \sqrt[3]{\alpha} + K_2 \left(1 - \frac{1}{3} \left(1 - \alpha\right)\right) + K_0
\]

In which \( K_0 \) equals the induction time \( (t_0) \). Schiller /4/ emphasizes that \( K_1 \) and \( K_2 \) have clearly defined physical meanings and are not just fitting parameters.

Schiller /4/ shows a number of simulations for the hydration of hemihydrate. In his simulations \( K_1 \) is between 21 - 48.3 minutes and \( K_2 \) from 11 to 21.6 minutes. Beretka and van der Touw /11/ used value for \( K_1 \) between 37.8 and 43.5 minutes and 15.1 - 30.3 minutes for \( K_2 \) for a mixture with wbr of 0.70. Fujii and Kondo /12/ used \( K_1 = 44 \) min and \( K_2 = 276 \) min for a wbr of 0.40. Although none of these authors specify the type of hemihydrate was used, from the hydration time one can conclude that \( \alpha \)-hemihydrate was involved. Singh and Middendorf /13/ point out that the induction period for \( \alpha \)-hemihydrate hydration is shorter than that for \( \beta \)-hemihydrate. But they also point out that \( \beta \)-hemihydrate hydrates faster because of its higher surface area which provides more nucleation sites for the crystallization of gypsum.
Analysis of measurements using the hydration model

In this subsection, the results of simulation based on the models are compared to the ultrasonic measurements. Therefore the model of Schiller is fitted to the experiments and the fitted parameters are analyzed.

The sound velocity graphs contain a series of characteristic important points. For instance, \( t_\tau = 0 \) is the point in time at which the sound velocity starts to increase. The time until this point is called the induction time. And \( t_\tau = 1 \) is the moment in time at which hydration is completed. These points can be directly related to the parameters of the Schiller model. \( K_0 \) is equal to \( t_\tau = 0 \) and \( K_0 + K_1 + K_2 \) equals to \( t_\tau = 1 \), see Eq. (5). Figure 1 shows both points in time for \( wbr = 0.80 \).

The exact determination of the value of \( t_\tau = 1 \) is challenging, since it requires that the moment of full hydration is clearly visible in the sound velocity graphs. Since this is not really the case, another method is applied here. In this method the time (\( t_\tau = 0.5 \)) needed to perform half of the hydration (\( \gamma = 0.5 \)) is determined. Based on Eq. (1), the sound velocity describing half hydration equals the average of the sound velocity of slurry and of hardened product. Table 1 and Figure 2 show the determined values for \( t_\tau = 0.5 \), based on the sound velocity curves.

<table>
<thead>
<tr>
<th>Mix</th>
<th>wbr</th>
<th>( \varphi_w )</th>
<th>( \varphi_{HH} )</th>
<th>( t_\tau = 0.5 )</th>
<th>( K_0 )</th>
<th>( K_1 )</th>
<th>( K_2 )</th>
<th>( t_\tau = 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.65</td>
<td>0.62</td>
<td>0.38</td>
<td>5.16</td>
<td>0.7</td>
<td>4.2</td>
<td>5.5</td>
<td>10.4</td>
</tr>
<tr>
<td>B</td>
<td>0.8</td>
<td>0.68</td>
<td>0.32</td>
<td>12.14</td>
<td>1.3</td>
<td>11.3</td>
<td>9.1</td>
<td>21.7</td>
</tr>
<tr>
<td>C</td>
<td>1.25</td>
<td>0.77</td>
<td>0.23</td>
<td>15.60</td>
<td>2.9</td>
<td>14.1</td>
<td>7.2</td>
<td>24.2</td>
</tr>
<tr>
<td>D</td>
<td>1.59</td>
<td>0.81</td>
<td>0.19</td>
<td>12.86</td>
<td>0.2</td>
<td>12.5</td>
<td>13.3</td>
<td>26.0</td>
</tr>
<tr>
<td>E</td>
<td>1.59acc</td>
<td>0.81</td>
<td>0.19</td>
<td>9.52</td>
<td>2.2</td>
<td>6.1</td>
<td>12.0</td>
<td>20.3</td>
</tr>
</tbody>
</table>

Table 1

Determined value for \( t_\tau = 0.5 \) and derived values for \( K_1 \) and \( K_2 \) by fitting
In order to determine the individual values of $K_0$, $K_1$, and $K_2$, the model is fitted to the experimental sound velocity curves taking into account the already determined values for $t_{in} = 0.5$. The fitting is performed by using the modified Schiller model (Eq. (36)) with $t_{in} = 0.5$. This modified model reads

$$t_{in} = K_1 \sqrt{0.5} + K_2 (1 - \sqrt{1 - 0.5}) + K_0 = (K_1 - K_2) \sqrt{0.5} + K_2 + K_0 \quad (6)$$

Table 1 and Figure 3 show the results of the fitting. From Figure 2, one can notice that the total time of hydration ($t_{in} = 1.0$) increased with an increasing water volume fraction in the mix. Both $K_1$ and $K_2$ seem linearly related to the volume fraction water, but these fits are not really conclusive. When neglecting the results of $wbr = 1.59$, there is a more clear trend visible. When doing this, $K_0$ and $K_1$ are related to the volume fraction water, while $K_2$ seems to be unrelated to this property. The neglect of $wbr = 1.59$ makes sense because the sound speed of the mixture is not in line with the rest of the measurements, as well as the position of the sound velocity curve.

The current research reveals the presence and magnitude of induction times ($K_0$ or $t_{in} = 0$), while Schiller /4/ neglects the induction time when applying his model. When comparing the derived value of $K_1$ and $K_2$ with the values given by Schiller /4/ and Beretka and van der Touw /11/, one can notice that here the values for $K_1$ and $K_2$ are...
lower. The lower values compared to literature /4, 11, 12/ can be explained by fact that these values were most probably determined for α-hemihydrate. While β-hemihydrate hydrates faster because of its larger surface area, which provides more nucleation sites for the crystallization of gypsum /13/. The nucleation of gypsum is, according to the model of Schiller, governed by $K_1$.

Literature does not provide additional information describing the effect of water/binder-ratio on $K_1$ and $K_2$, neither for α- nor β-hemihydrate. A research by Smith et al. /1/ on the hydration of calcium aluminate cement using the Schiller model showed a relation between $K_1$ and water binder ratio, while the value of $K_2$ was constant within a narrow water/binder ratio range. The current research shows partly the same positive relation between $K_1$ and water/binder-ratio, especially when neglecting the measurement with water/binder ratio of 1.59. Furthermore, also here a quite constant value of $K_2$ is observed.

**Conclusions**

It is shown in the previous section that the relation between hydration degree and sound velocity as given by Smith et al. /1/ is applicable for the hydration of hemihydrate. Within this model the equations of Robeyst et al. /2/ and Ye /3/ can be used to describe the sound velocity at the start and end, respectively, of the hydration process.

Furthermore the hydration model of Schiller is applied on the ultrasonic sound velocity measurements. A fitting of the Schiller /4/ model to the experimental results has been performed using the $t_{0.5}$-method. The analysis of the results showed that $K_0$ and $K_1$ are linearly dependent on the water/binder-ratio, while $K_2$ is unrelated to the water/binder ratio. $K_0$, $K_1$ and $K_2$ describe the induction time, the gypsum growth and the hemihydrates dissolution, respectively. Furthermore it is noticed that the induction time ($t_{0.5}$ or $K_0$) is linearly related to the volume fraction water, and therefore directly related to the water/binder ratio.

The model of Robeyst et al. /2/ for the sound velocity of a slurry showed a good agreement with the experimental values, when taking into account an air content up to 1.7%. This model is based on the theoretical model of Harker and Temple /14/ for ultrasonic propagation in colloids. It takes into account the bulk moduli of the continuous (fluid) and discontinuous (solid) phase as well as the size and shape of the solid particles. The bulk modulus of the fluid is corrected for the presence of entrapped air by the use of Eq. (14) /15/. The effect of size and shape of the particles are described by Harker and Temple /14/.

A very good agreement for porous materials was found between the experimental and theoretical values with ‘direct’ methods. These methods use fixed sound velocities for the different phases against of sound velocity of the phases based on the bulk and shear moduli with the ‘indirect’ methods. From these ‘direct’ methods the series arrangement according to Ye /3/ (Eq. (30)) with $c_s = 6800 \, \text{m/s}$ for gypsum gave the best results. Reverse analysis showed that the difference in the prediction of void fraction are in the range of +1.4% and -2.4%. Also a good agreement is found with the equation of Dalui et al. /16/ (Eq. (27)) with $n = 0.84$ and $c_0 = 4571$ for the lower void fractions.

The ultrasonic sound velocity through the hydrating material could be related to the hydration curve. It is shown that this is possible using the combination of the hydration model of Schiller /4/ and the relation between hydration degree and sound velocity given by Smith et al. /1/. A fitting of the Schiller model to the experimental sound
velocity curves for the different employed water/binder-ratios has been performed. Analysis of the fitting results showed that the parameters $K_0$ and $K_1$ are positively and linearly related to the water/binder ratio. The parameter $K_2$ is unrelated to the volume fraction water.

**References**


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