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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

$$\alpha = \frac{c_e - c_{sl}}{c_{hp} - c_{sl}} + \alpha_0 \qquad (1)$$

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 α_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;

$$\frac{1}{c_{sl}^2} = \left(\left(1 - \frac{c_{air}}{\varphi_t} \right) \frac{\varphi_t}{K_w} + \frac{c_{air}}{\varphi_t} \frac{\varphi_t}{K_{air}} + \frac{(1-\varphi_t)}{K_{HH}} \right) \cdot$$
$$\left(\frac{\rho_f \left(\rho_{HH} \left(\varphi_t + \frac{(1-\varphi_t)}{2} \left(\frac{1+2(1-\varphi_t)}{\varphi_t} \right) \right) + \frac{1}{2} \rho_f (1+2(1-\varphi_t)) \right)}{\rho_{HH}\varphi_t^2 + \rho_f \left(\frac{1}{2} \left(\frac{1+2(1-\varphi_t)}{\varphi_t} \right) + \varphi_t(1-\varphi_t) \right)} \right) \qquad (2)$$

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

$$c_{hp} = \frac{c_{DH} c_f}{(1-\varphi_t) c_f + \varphi_t c_{DH}} \qquad (3)$$

Finally, Eq. (1) can be rewritten to

$$c_e = \alpha (c_{hp} - c_{sl}) + c_{sl} \qquad (4)$$

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

$$t = K_1 \sqrt[3]{\alpha} + K_2 \left(1 - \sqrt[3]{1-\alpha} \right) + K_0 \qquad (5)$$

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 α-hemihydrate was involved. Singh and Middendorf /13/ point out that the induction period for α-hemihydrate hydration is shorter than that for β-hemihydrate. But they also point out that β-hemihydrate hydrates faster because of its higher surface area which provides more nucleation sites for the crystallization of gypsum.
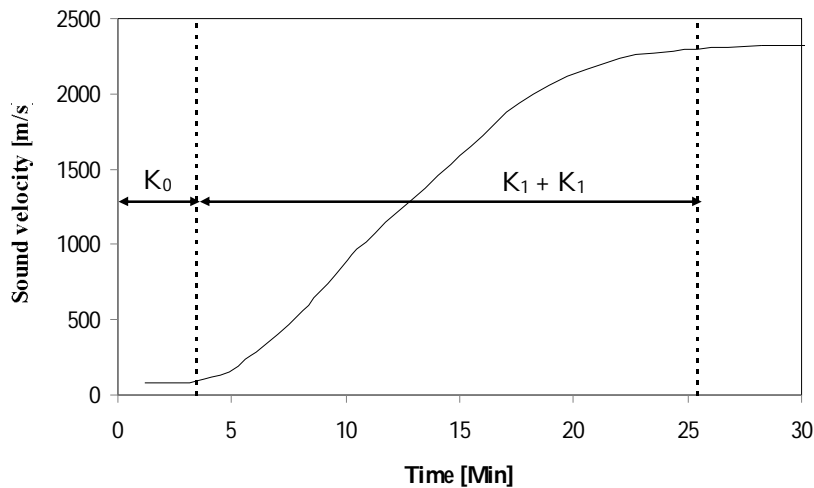
Figure 1

Determination of K_0 and $K_1 + K_2$ for experimental results with wbr = 0.80.

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 serie of characteristic important points. For instance, $t_{\alpha=0}$ is the point in time at which the sound velocity starts to increase. The time until this point is called the induction time. And $t_{\alpha=1}$ 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 $t_{\alpha=0}$ and $K_0 + K_1 + K_2$ equals to $t_{\alpha=1}$, see Eq. (5). Figure 1 shows both points in time for wbr = 0.80.

The exact determination of the value of $t_{\alpha=1}$ 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 ($t_{\alpha=0.5}$) needed to perform half of the hydration ($\alpha = 0.5$) 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 $t_{\alpha=0.5}$, based on the sound velocity curves.

Mix	wbr	φ_w	φ_{HH}	$t_{\alpha=0.5}$	K_0	K_1	K_2	$t_{\alpha=1}$
A	0.65	0.62	0.38	5.16	0.7	4.2	5.5	10.4
B	0.8	0.68	0.32	12.14	1.3	11.3	9.1	21.7
C	1.25	0.77	0.23	15.60	2.9	14.1	7.2	24.2
D	1.59	0.81	0.19	12.86	0.2	12.5	13.3	26.0
E	1.59[acc]	0.81	0.19	9.52	2.2	6.1	12.0	20.3

Table 1

Determined value for $t_{\alpha=0.5}$ and derived values for K_1 and K_2 by fitting
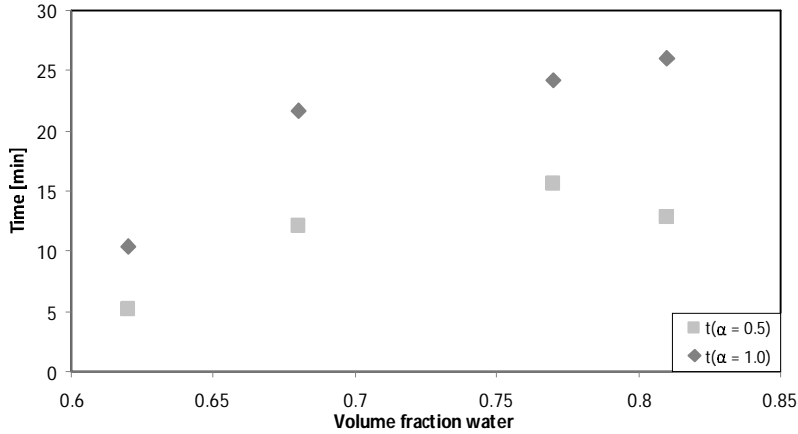
Figure 2

Determined values of $t_{\alpha=0.5}$ and $t_{\alpha=1}$ (K_0 + K_1 + K_2) versus initial volume fraction water
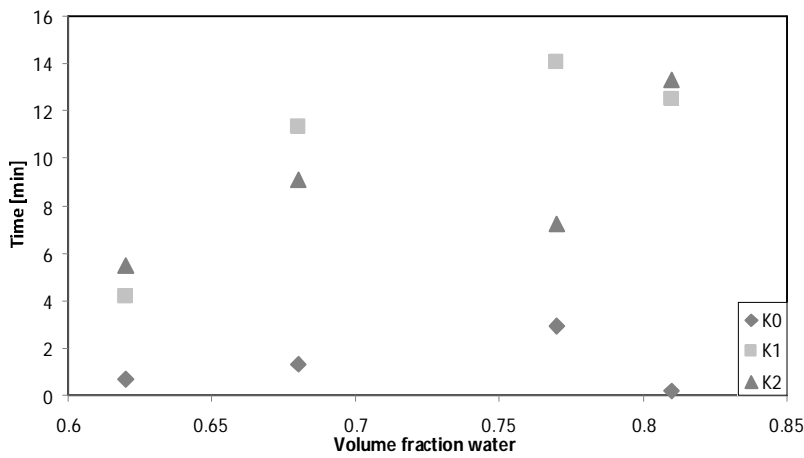

Figure 3

Derived values of K_0 ($t_{\alpha=0}$), K_1 and K_2 by fitting of the experimental and simulated sound velocity curves without accelerator

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 $t_{\alpha=0.5}$. The fitting is performed by using the modified Schiller model (Eq. (36)) with $t_{\alpha=0.5}$. This modified model reads

$$t_{\alpha=0.5} = K_1\sqrt[3]{0.5} + K_2(1-\sqrt[3]{1-0.5}) + K_0 = (K_1 - K_2)\sqrt[3]{0.5} + K_2 + K_0 \qquad (6)$$

Table 1 and Figure 3 show the results of the fitting. From Figure 2, one can notice that the total time of hydration ($t_{\alpha=1.0}$) 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 $t_{\alpha=0}$), 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 $t_{\alpha=0.5}$-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 ($t_{\alpha=0}$ 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 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.

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