Ultrasonic sound speed measurement as method for the determining the hydration degree of gypsum

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Abstract
This article addresses the sound velocity through slurries as well as non-porous and porous materials. The focus is on using the sound velocity for the microstructure prediction of porous materials, especially gypsum plasterboards, during and after hydration.

For a slurry, the model of Robeyst et al. [1] showed a good agreement with experimental data when taking into account an air content of 10 ml per kg of hemi-hydrate. This model 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.

For gypsum materials, the best agreement was found between the experimental and theoretical values using a series arrangement according to Ye [2] with a solid sound velocity (c_s) of 6800 m/s.

Finally, the sound velocity during the hydration of gypsum is studied. The use of linear relation between the amount of hydration-product (gypsum) formed and sound velocity gives a reasonable result. Furthermore a relation between initial volume fraction hemihydrate and hydration time is shown.

1. Introduction

The purpose of this research is to relate ultrasonic velocity through a mix to the hydration of β-hemihydrate. The sound velocity of 4 water/gypsum ratios are used during the experiments. Table 1 shows the mix designs, the calculated void fractions of the mixtures in this research based on the model of Brouwers [3] and the measured ultrasonic velocity [4]. The used β–hemihydrate and the measuring method are described in detail in De Korte and Brouwers [5].

Table 1, Mix designs, computed void fractions [3] and the results of the ultrasoon measurements [4]

	Mix design			
	A	**B**	**C**	**D**
Water/hemihydrate ratio	0.63	0.8	1.25	1.59
Before hydration				
Computed void fraction	0.624	0.678	0.767	0.807
Measured sound velocity	75	85	134	134
After hydration				
Computed void fraction	0.493	0.566	0.685	0.740
Measured sound velocity	2500	2300	2000	3172

2. Sound velocity of slurries and porous media

This section will describe a model for the sound velocity in slurry and two methods for the calculation of the sound velocity of a porous material as well as the results of different methods.

2.1 Sound velocity of slurry

This sub-section describes the sound velocity of slurry with and without entrapped air. Robeyst et al. [1] presents a model for ultrasonic velocity through fresh cement mixtures, based on the theoretical model of Harker and Temple [6] for ultrasonic propagation in colloids. According to these models, the effective wave velocity (c_e) in a suspension is given by;

$$c_e^2 = \left[\left(\varphi_t \frac{1}{K_f} + (1-\varphi_t)\frac{1}{K_s}\right)\left(\frac{\rho_f\left(\rho_s\left(\varphi_t + (1-\varphi_t)S\right) + \rho_f S\varphi_t\right)}{\rho_s\varphi_t^2 + \rho_f\left(S + \varphi_t(1-\varphi_t)\right)}\right)\right]^{-1} \quad (1)$$

with the subscript f refers to the fluid and s to the solid. Where, the parameter S generally depends on the size and shape of the particles, the void fraction and the continous phase viscosity [7], but it can be approximated by Eq. (2) for spherical particle in a fluid [8]

$$S = \frac{1}{2}\left(\frac{1+2(1-\varphi_t)}{\varphi_t}\right) \quad (2)$$

When the air is entrapped in the continuous fluid, the compressibility of the continuous phase can be corrected the air assumed to be uniformly distributed

$$\frac{1}{K_f} = \left(1 - \frac{c_{air}}{\varphi_t}\right)\frac{1}{K_{water}} + \frac{c_{air}}{\varphi_t}\frac{1}{K_{air}} \quad (3)$$

with c_{air} is the air content of the fluid and K_{air} is the bulk modulus of air. The calculated sound velocities with Eq. (1) are much higher than the measured sound velocity during the experiments. The main reason for this is the overestimation of the bulk modulus of the continuous fluid as described by Robeyst et al. [1]. Therefore the bulk modulus of the fluid is corrected with Eq. (3), with the bulk modulus of air 142 kPa and the bulk modulus of water 2.2 GPa. Based on this equation, the air content of the pore fluid can be derived. A typical value of 2.7% ($V_{air}/V_{hemihydrate}$) or 10 ml air per kg hemihydrate is found in this research.

2.2 Sound velocity of solid

The sound velocity of a porous material can also calculated directly from the individual sound velocities of the individual phases. Dalui et al. [9] used a simple equation to predict the effective sound speed in a porous medium. This equation reads

$$c_e = c_s(1-\varphi_t)^n \quad (4)$$

with n being an empirical constant, c_s is the sound speed in the non-porous material and φ is the void fraction. Dalui et al. [9] propose $n = 0.84$ and $c_s = 4571$ m/s. Eqs. (4) is based on a parallel arrangement. Another possibility is to use a serie arrangement as derived by Ye [2], and the equation for this arrangement reads

$$c_e = \frac{c_s c_f}{(1-\varphi_t)c_f + \varphi_t c_s} \tag{5}$$

with c_e is the effective velocity, c_s the velocity of the solid phase, c_f the velocity of the fluid and φ_t the void fraction. The results of Equation (4)-(5) are shown in Table 2. The predicted values based on Eq. (5) are close to the experimental value for all water-gypsum ratios. For the lowest water-gypsum ratios the predictions are too low, will for the higher water-gypsum ratios the prediction tends to overestimate the velocity. The best results for Eq. (5) are found with the solid sound velocity of 6800 m/s.

Table 2: Results of the direct method

	c_s	**A**	**B**	**C**	**D**
Water/gypsum ratio		0.63	0.8	1.25	1.59
Void fraction		0.493	0.566	0.685	0.74
Measured		2500	2300	2000	1835
Eq. (4)	6800	3843	3373	2577	2193
Eq. (5)	6800	2476	2263	1985	1878
Eq. (5)	5440	2367	2184	1939	1845
Eq. (5)	4571	2271	2114	1899	1814

3. Velocity during hydration process

In the previous sections the ultrasonic measurements are compared with the prediction based on the theoretical equations. Based on the results we are now able to predict two points during the hydration process, namely the starting and finishing point of the hydration. Currently the process in between is not described. This section will describe the stage between begin and end point as well as a model to relate hydration degree to time.

3.1 Relation between hydration degree and sound velocity

Smith et al. [10] describes the relation between hydration mechanism and ultrasonic measurements in aluminous cement. They provide a correlation between hydration degree and ultrasonic measurements. This correlation reads;

$$\alpha = \frac{c_e - c_0}{c_1 - c_0} + \alpha_0 \tag{6}$$

With c_e is the measured sound velocity through mix, c_0 is the sound velocity at moment the velocity starts increasing (so, of the slurry), c_1 is the sound velocity when the velocity decreases again (so, of the hardened product) and α_0 is the hydration degree at moment of c_0 (which is here zero). The sound velocity of the slurry is given by Robeyst et al. [1] (Eq. (1)). The sound velocity of the hardened product can be described with Ye [2] (Eq. (5)). Eq. (6) can be rewritten to

$$c_e = \alpha(c_{hp} - c_{sl}) + c_{sl} \tag{7}$$

3.2 Analytical hydration models

In this section, analytical hydration models are described. The purpose is to relate the hydration degree to time. In literature several different hydration models have been introduced. The model of Schiller [11] has the advantage that it indirectly includes water/gypsum ratio in the parameters. The equation of Schiller [11] reads

$$t = K_1\sqrt[3]{\alpha} + K_2\left(1 - \sqrt[3]{1-\alpha}\right) + K_0 \tag{8}$$

In which K_0 equals the induction time ($t_{\alpha=0}$). Schiller [11] emphasizes that K_1 and K_2 have clearly defined physical meanings and are not just fitting parameters.

Schiller [11] shows a number of simulations for the hydration of hemihydrate. In his simulations K_1 is between 21 - 48.3 minute and K_2 from 11 to 21.6 minute. Beretka and van der Touw [12] 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 wgr of 0.70. Fujii and Kondo [13] used $K_1 = 44$ min and $K_2 = 276$ min for a water/gypsum-ratio of 0.40. Although none of these authors specify the type of hemihydrate was used, one could assume α-hemihydrate based on the hydration speed. Singh and Middendorf [14] point out that the induction period for α-hemihydrate hydration is shorter than that for β-hemihydrate. But the β-hemihydrate hydrates faster because of its higher surface area which provides more nucleation sites for the crystallization of gypsum.

3.3 Analysis measurements with hydration model

In this subsection, the results of simulation based on the models of Sections 2.1 and 2.2 are compared to the measurements of Section 3. Therefore the the model of Schiller is fitted to the experiments and the fitted parameters are analyzed.

The sound velocity graphs contains a serie of important points. $t_{\alpha = 0}$ is the point in time at which the sound velocity starts to increase. The time until this point is called the induction time. $t_{\alpha = 1}$ is the moment in time at which hydration is completed. These points can be related to the Schiller model. K_0 is equal to $t_{\alpha = 0}$ and $K_0 + K_1 + K_2$ equals to $t_{\alpha = 1}$.
The exact determination of the value of $t_{\alpha = 1}$ is challenging, since it assumed that the moment of full hydration is clearly visible in the sound velocity graphs. Since this is not complete clear, 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. (7) [10], the sound velocity describing half hydration equals the average of the sound velocity of slurry and of hardened product.
Figure 1a shows the determined values for K_0 and $t_{\alpha = 0.5}$ based on the sound velocity curves. From Figure 1a, one can notice that there is a linear relation between volume fraction water and initial setting time ($t_{\alpha=0}$).
In order to determine the value of K_1 and K_2 separately, the simulation is fitted to the experimental sound velocity curves taking into account the already determined values for K_0 and $t_{\alpha=0.5}$, The fitting is performed by using the modified Schiller model (Eq. (35)) with $t_{\alpha = 0.5}$. This modified model reads

$$t_{a=0.5} = K_1\sqrt[3]{0.5} + K_2(1 - \sqrt[3]{1-0.5}) + K_0 = (K_1 - K_2)\sqrt[3]{0.5} + K_2 + K_0 \tag{9}$$

Figure 1b shows the results of the fitting. Both K_1 and K_2 seems to be related to the volume fraction water. When comparing the derived value of K_1 and K_2 with the values given by Schiller [11] and Beretka and van der Touw [12], one can notice that the values for K_1 are much lower and the value for K_2 are comparable. The lower values for K_1 compared to literature [11],[12],[15] can be explained by fact that these value were most probably for α-hemihydrate. While β-hemihydrate hydrates faster because of its higher surface area which provides more nucleation sites for the crystallization of gypsum [14]. The nucleation of gypsum is described by K_1 according to the model of Schiller.

An extensive literature search did not lead to any literature describing the effect of water/gypsum-ratio on K_1 and K_2 for neither α- nor β-hemihydrate. A research on the hydration of calcium aluminate cement using the Schiller model by Smith et al. [10] showed a relation between K_1 and water binder ratio, while the value of K_2 was constant within small water-binder ratio range. The current research shows partly the same positive relation between K_1 and water/gypsum-ratio.

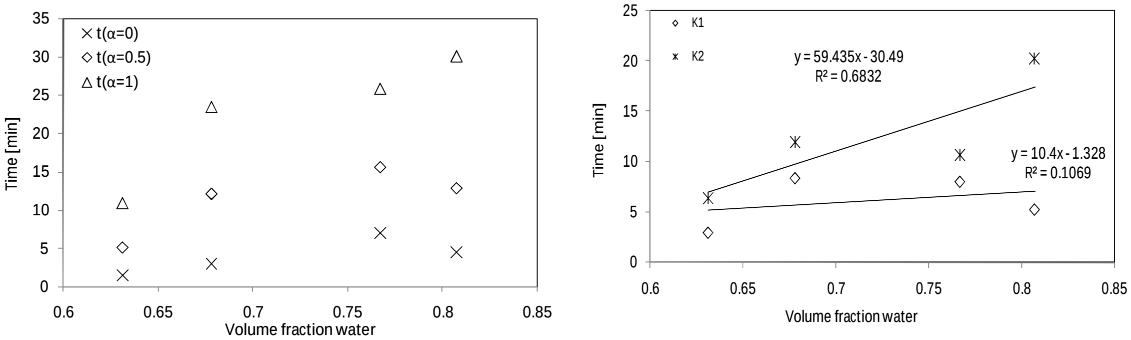

Figure 1 (a) Determined value of induction time ($t_{\alpha=0}$), $t_{\alpha=0.5}$, and full hydration time ($t_{\alpha=1}$) (b) Derived value of K_1 and K_2

4. Conclusions

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

Furthermore the hydration model of Schiller is applied on the ultrasonic sound velocity measurements. A fitting of the Schiller model on the experimental results has been performed using the $t_{\alpha=0.5}$-method. The analysis of the results showed that both parameters K_1 and K_2 are linearly dependent of the water/gypsum-ratio. K_1 and K_2 describe the gypsum growth and the hemihydrates dissolution, respectively. Furthermore it is noticed that the induction time ($t_{\alpha=0}$ or K_0) is linear related to the volume fraction water.

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