Abstract
This article focuses on the computation of the sound velocity through slurries and hardened products. The purpose is to use the sound velocity to quantify the composition of the fresh slurry as well as the hardening and hardened - porous - material. Therefore the volumetric models for hydration of calcium sulphates given by Brouwers /1/ is integrated with sound velocity equations found in literature. Furthermore the derived model is compared with experimental data. This shows that the model of Robeyst et al. /2/ gives good results for the computation of sound velocity through slurries, while the model of Ye /3/ give good results for the computation of sound velocity through hardened porous material.

Introduction
Currently the hydration of hemihydrate to gypsum and cement is studied by IR, SEM and Vicat techniques. Because the speed of hydration is more difficult to measure the hydration curve and the different processes which take place. For the measurement of the hydration of cement and concrete in the last decade ultrasonic sound velocity measurements have been applied successfully /2, 4, 5/. This method has the advantage over the more traditional methods, such as the aforementioned Vicat-needle, SEM and IR, that ultrasonic measurements are continuous /6/, and that it provides information about the microstructure development and the related properties like strength development /2/. Especially for hemihydrate hydration, due to the short hydration time, is difficult to stop the hydration for discontinuous measurements. The ultrasonic sound velocity method used here is developed and patented by the University of Stuttgart /7/. This article will focus on the application of the ultrasonic sound velocity measurement for assessing the hydration curve of hemihydrate to gypsum. Therefore it will be combined with information about the volume fractions of binders and hardened material during hydration and the classic hydration-time relations given by Schiller /8/.

Sound velocity of materials
There are two methods to obtain the sound speed of the materials. The first method is the use of values from literature. Table 1 shows the sound speed through some materials. Besides this method, there is a second method to acquire the value of sound speed. This method is based on the elastic modulus and density of the material and reads

\[ c = \sqrt{\frac{K}{\rho}} \]  

(1)
Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific density (kg/m³)</th>
<th>Sound speed (m/s)</th>
<th>Elastic modulus (GPa)</th>
<th>Bulk modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Poisson ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1000</td>
<td>1497</td>
<td></td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>346</td>
<td></td>
<td></td>
<td>0.142</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel</td>
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<td>5930</td>
<td>170</td>
<td>79.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dihydrate</td>
<td>2310</td>
<td>6800</td>
<td>45.7</td>
<td>42.5-45.7</td>
<td>15.7-17</td>
<td>0.33</td>
</tr>
<tr>
<td>Hemihydrate</td>
<td>2619</td>
<td>62.9</td>
<td>52.4</td>
<td>24.2</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Anhydrit</td>
<td>2520</td>
<td>80</td>
<td>54.9</td>
<td>29.3</td>
<td>0.275</td>
<td></td>
</tr>
</tbody>
</table>

with \( c \) the sound speed, \( K \) the bulk modulus and \( \rho \) the specific density. This method is suitable for fluids and gases, but is not valid for solid materials. For example, for steel \( K = 170 \) GPa and \( \rho = 7700 \) kg/m³, yielding a sound velocity of 4699 m/s, while commonly accepted value of its sound speed is 5930 m/s /14/. Kinsler /14/ points out that the computational method will deliver the so-called bar sound speed. This is caused by the fact that solids can support two types of elastic waves (e.g. longitudinal and shear). In an isotropic solid of which the dimensions are much larger than the wavelength of the acoustic wave, the appropriate speed for the longitudinal waves is the bulk speed /14/. The bulk speed is for all materials larger than the bar speed of the same material. The equation for the bulk speed reads

\[
c_{\text{long}} = \sqrt{\frac{K + \frac{4}{3}G}{\rho}} \tag{2}
\]

Where \( K \) and \( G \) are the bulk and shear modulus of the solid, respectively, and \( \rho \) its density. The shear modulus of steel is 79.3 GPa. This yields to sound speed of 5980 m/s, which is close to the commonly accepted value of 5930 m/s. Besides the speed in longitudinal direction, there is also a speed in the shear direction. The equation for this direction reads

\[
c_{\text{shear}} = \sqrt{\frac{G}{\rho}} \tag{3}
\]

Table 1 shows the elastic, bulk and shear modulus of several materials, as well as that of water and air. When applying Eq. (1) and (2), the results for (non-porous) gypsum are 4289-4448 m/s, and 5019-5210 m/s, respectively. The results of both equations are lower than the experimental value of 6800 m/s provided by Losso and Viveiros /9/. The shear velocity according to Eq. (3) is 2607-2712 m/s.

So the Eqs. (1)-(3) are applicable for fluids, but are not suitable for solids, since they tend to underestimate the sound velocity through solids. This is even more true for porous solids, which also contain voids. In the next section the composition of a hemihydrates-water-gypsum is addressed, used here for the development of a new model relating sound velocity and compositional properties.
Experiments

Materials

Within this research β-hemihydrate is used as the binder. The hemihydrate used during the experiments was produced from flue gas desulphurization gypsum, which is commonly used for the production of gypsum plasterboards. The particle size distribution (PSD) is shown in Figure 1. The used β-hemihydrate consists of 97% pure hemihydrate and 3% other compounds /15/. The hemihydrate has a Blaine value of 3025 cm$^2$/g and a density of 2619 kg/m$^3$. The Blaine value describes the fineness of the binder particle (hemihydrate). Hunger and Brouwers /16/ point out that the Blaine test methods are not applicable for powders with higher fineness (i.e. particles $<$ 10 µm). The hemihydrates used, has 35% of the particles smaller than 10 µm, therefore the Blaine value is less suitable. Another method to determine the fineness of powder is the use of specific surface area (SSA). Hunger /17/ showed a method to calculate the specific surface area based on the PSD. Hunger and Brouwers /16/ showed that there is a constant ratio between Blaine value and computed SSA. The Blaine value has to be multiplied by about 1.7 to obtain the SSA. Applied here, the SSA based on the given Blaine value would amount 5130 cm$^2$/g. The computation of the SSA using the PSD depends on the shape of the particles. For spheres the shape factor equals unity. Using this shape factor, the SSA of the used hemihydrate would be 3771 cm$^2$/g. However, these powder particles are not spherical, and the amount of specific surface area is higher. To match computed SSA and Blaine value of 5130 cm$^2$/g, here a shape-factor of 1.36 follows for β-hemihydrate. It is noteworthy that Hunger and Brouwers /16/ found a shape-factor of 1.18 for α-hemihydrate.

Measurements

The measurements were executed at the Materialprüfungsanstalt of the University of Stuttgart (Germany). The sound velocity of 4 water/binder ratios is measured during the experiments. The 4 water/binder-ratios (wbr) are 0.63, 0.80, 1.25 and 1.59. Besides these four mixtures also a mixture with wbr of 1.59 with 0.40 % (m/m) accelerator is tested. Table 3 shows the mix-designs used during the experiments. Figure 2 shows the measured sound velocity during hydration of the 4 mixtures.
The hemihydrate hydration experiments with ultrasonic method were performed using the FreshCon system which was developed at the University of Stuttgart. The measurements are performed in a container. Which consists of two polymethacrylate walls and u-shaped rubber foam element in the center, which are tied together by four screws with spacers. The volume of the mold is approximately 45 cm³ for the test. The measurements were performed with use of two Panametrics V106, 2.25MHz centre frequency sensors. For the processing of the measuring data during the experiments, in-house developed software (FRESHCON2) is used. More detailed information about the FreshCon system and the measurement procedure can be found in Reinhardt and Grosse /4/.

<table>
<thead>
<tr>
<th>Mix design</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/hemihydrate ratio</td>
<td>0.63</td>
<td>0.8</td>
<td>1.25</td>
<td>1.59</td>
<td>1.59</td>
</tr>
<tr>
<td>Accelerator (m/m on hemihydrates)</td>
<td></td>
<td></td>
<td></td>
<td>0.40%</td>
<td></td>
</tr>
<tr>
<td>Before hydration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Computed void fraction</td>
<td>0.624</td>
<td>0.678</td>
<td>0.767</td>
<td>0.807</td>
<td>0.807</td>
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<td>Measured sound velocity (m/s)</td>
<td>75</td>
<td>85</td>
<td>134</td>
<td>223</td>
<td>134</td>
</tr>
<tr>
<td>After hydration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Computed void fraction</td>
<td>0.493</td>
<td>0.566</td>
<td>0.685</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>Measured sound velocity (m/s)</td>
<td>2500</td>
<td>2300</td>
<td>2000</td>
<td>3172</td>
<td>1835</td>
</tr>
</tbody>
</table>

Table 2
Mix designs, computed void fractions based on Brouwers /1/ and the results of the ultrasound measurements /18/

Figure 2
Measured sound velocity by Grosse and Lehmann /18/
The calculated void fractions of the mixtures in this research, based on the model of Brouwers /1/, are given in Table 3. Table 3 also shows the measured ultrasonic velocity by Grosse and Lehmann /18/. Figures 3 and 4 are graphic representations of the sound velocity data versus computed void fraction from Table 3. It can be noticed from the figures that there is a clear relation between void fraction and velocity as well before as after hydration, so $\alpha = 0$ and $\alpha = 1$, respectively. But the trend is exactly opposite before and after hydration. Before hydration the velocity increases with increasing void fraction (i.e. water content), while the velocity is decreasing with increasing void fraction after hydration. In the next section relations will be established between the volumetric composition ($\alpha = 0$ and $\alpha = 1$) and sound velocity.

**Sound velocity of slurries and porous media**

**Sound velocity of a slurry**

This sub-section describes the sound velocity of a slurry, i.e. a suspension, containing entrapped air. Robeyst et al. /2/ presented a model for ultrasonic velocity through fresh cement mixtures, based on the theoretical model of Harker and Temple /19/ for
ultrasonic propagation in colloids. According to these models, the effective wave velocity \( c_e \) in a suspension is given by:

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

With the subscript f referring to the fluid and s to the solid, and \( \phi_t \) to the fluid volume fraction. The parameter \( S \) generally depends on the size and shape of the particles, the void fraction and the continuous phase viscosity /20/, but it can be approximated for spherical particles in a fluid /21/ as

\[
S = \frac{1}{2} \left( 1 + \frac{2(1 - \phi_t)}{\phi_t} \right)
\]

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

\[
\frac{1}{K_f} = \left( 1 - \frac{c_{\text{ar}}}{\phi_t} \right) \frac{1}{K_{\text{water}}} + \frac{c_{\text{ar}}}{\phi_t} \frac{1}{K_{\text{air}}}
\]

With \( c_{\text{ar}} \) as the air volume fraction in the voids of the fluid and \( K_{\text{air}} \) the bulk modulus of air.

**Sound velocity of solid**

The sound velocity of a porous material can also calculated directly from the individual sound velocities of the individual phases. Roth et al. /22/ used a simple equation to predict the effective sound speed in a porous medium. This equation reads

\[
c_e = c_s (1 - \phi_t)
\]

With \( c_s \) the sound speed in the non-porous material and \( \phi_t \) the void fraction. Dalui et al. /23/ have added an exponent

\[
c_e = c_s (1 - \phi_t)^n
\]

With exponent \( n \) being an empirical constant. For \( \alpha \)-hemihydrate, Dalui et al. /23/ proposed \( n = 0.84 \) and \( c_s = 4571 \text{ m/s} \).  

60
A drawback of these empirical equations is that in the limit of the void fraction approaching unity, a sound velocity of zero is obtained, which is obviously not correct. Therefore, here an additional term is added to Eq. (7) and (8) which takes in account the sound velocity of the fluid:

$$c_e = c_s (1 - \phi_t) + c_f \phi_t$$  \hspace{1cm} (9)

and

$$c_e = c_s (1 - \phi_t)^n + c_f \phi_t^n$$  \hspace{1cm} (10)

With $c_s$ being the sound speed of the fluid. Eqs. (7)-(10) are based on a parallel arrangement. Another possibility is to use a series arrangement /3/, and the equation for this arrangement reads

$$c_e = \frac{c_s c_f}{(1 - \phi_t) c_f + \phi_t c_s}$$  \hspace{1cm} (11)

With $c_e$ as the effective velocity, $c_s$ the velocity of the solid phase, $c_f$ the velocity of the fluid and $\phi_t$ the void fraction.

**Applying the volumetric models to sound velocity measurements**

**Sound velocity of a slurry**

Table 3 shows the results of Eq. (4) with $K_s = 52.4$ GPa, $K_f = 2.2$ GPa (Table 1). The calculated sound velocities with Eq. (4) are much higher than the measured sound velocity during the experiments. The main reason for this is the overestimation of the fluid bulk modulus as described by Robeyst et al. /2/. Therefore the bulk modulus of the fluid is corrected with Eq. (6), with the bulk modulus of air 142 kPa and the bulk modulus of water 2.2 GPa (Table 1). Based on this equation, the air content ($C_{air}$) of the pore fluid can be derived, which is included in Table 3.

Further computations reveal that the volume fraction air divided by the volume fraction of the binder in the slurry lies in a very small range (Table 3). This could indicate that air entered the slurry on the surface of the hemihydrate particles and a typical value is thus 2.7% (V/V) or 10 ml air per kg hemihydrate. Given the Blaine value of 3025 cm$^2$/g, this would mean $3.28 \times 10^{-5}$ ml air per cm$^2$ hemihydrate surface (= $3.28 \times 10^{-2}$ ml/m$^2$), corresponding to an air layer thickness of 32.8 nm.
Table 4

<table>
<thead>
<tr>
<th>Water/binder ratio (m/s)</th>
<th>C</th>
<th>A</th>
<th>B</th>
<th>E</th>
<th>D</th>
<th>Table 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water/binder ratio</td>
<td>0.63</td>
<td>0.8</td>
<td>1.25</td>
<td>1.59</td>
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</tr>
<tr>
<td>Accelerator</td>
<td>0.40%</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Void fraction</td>
<td>0.493</td>
<td>0.566</td>
<td>0.685</td>
<td>0.74</td>
<td>0.74</td>
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<tr>
<td>Measured</td>
<td>2500</td>
<td>2300</td>
<td>2000</td>
<td>3172</td>
<td>1835</td>
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</tr>
<tr>
<td>Direct method</td>
<td>Eq. (7)</td>
<td>6800</td>
<td>3448</td>
<td>2951</td>
<td>2142</td>
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<td>Eq. (8)</td>
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<td>Eq. (9)</td>
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<td>Eq. (11)</td>
<td>4571</td>
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<td>2114</td>
<td>1899</td>
<td>1814</td>
</tr>
</tbody>
</table>

Results of the direct method (Eqs (7)-(11)) with sound velocity (m/s), specific density (kg/m³), bulk moduli (GPa), shear moduli (GPa) and poison ratio (-) according to Table 1.

Sound velocity of solid
The results of Equation (7)-(10) are shown in Table 4. It can be noticed that the predicted values based on Eq. (7) differ from the measured values. Eq. (30) results in a too high velocity for all measurements when using the sound speed of 6800 m/s for gypsum (Table 1). When using 4571 m/s as sound velocity of gypsum as given by Dalui et al. /23/, the measurements for the first two experiments show good agreement. But the values for the mixtures with higher water/binder ratio (e.g. higher void fraction) are too low. Both Eq. (9) and (10) lead to an overestimation compared with the experimental value.

The predicted values based on Eq. (11) are close to the experimental values for all water/binder ratios. For the lowest water/binder ratios the predictions are too low, while for the higher water/binder ratios the prediction tends to overestimate the velocity. The best results for Eq. (7) are found with the solid sound velocity of 6800 m/s.

Conclusions
The model given by Robeyst et al. /2/ for predicting the sound velocity of slurry shows a good fit in the experiments assuming a constant air content of 2.7% (V/V) based on the volume of hemihydrate. In case of the hardened (porous) material, the closest fit between experimental and predicted value is found by the use of the direct method. The best results were obtained with the series arrangement based on the empirical sound velocity values; Eq. (11) with $c_s = 6800$ m/s and $c_f = 1497$. Also the equation of Dalui et al. /23/ (Eq. (8)) shows a good agreement for the two lowest void fractions, using with $c_s = 4571$ m/s and $n = 0.84$. 

62
References
/16/ M. Hunger and H. J. H. Brouwers, “Flow analysis of water-powder mixtures: Application to specific surface area and shape factor,” Cement and Concrete


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