Q.L. Yu; H.J.H. Brouwers; A.C.J. de Korte

Gypsum hydration: a theoretical and experimental study

Calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$ or gypsum) is used widely as building material because of its excellent fire resistance, aesthetics, and low price. Hemihydrate occurs in two formations of α- and β-type. Among them β-hemihydrate is mainly used to produce gypsum plasterboard since the hydration product of the α-hemihydrate is too brittle to be used as building material /10/. This article addresses the hydration of hemihydrate since it determines the properties of gypsum and it is influenced strongly by water and the properties of hemihydrate. The microstructure development of gypsum during hydration is investigated. The influence of water is studied from its effect on fresh behavior and void fraction of the gypsum.

Hydration of hemihydrates

Hemihydrate takes place hydration reaction immediately after mixing with water according to a through-solution route, first the hemihydrate dissolves and then the dihydrate precipitates from the solution.

$$CaSO_4 \cdot 0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{1}$$

The hydration of two hemihydrates (α- and β-), produced from flue gas desulfurization gypsum, from Knauf Gips KG was investigated. The particle size distribution that was measured with Mastersizer 2000 is shown in Figure 1. Results show that the mean particle size of α-hemihydrate is larger than that of β-hemihydrate, which is in line with /9/ that α-hemihydrate consists of large primary particles while β-hemihydrate forms flaky, rugged secondary particles with scanning electron micrograph method.

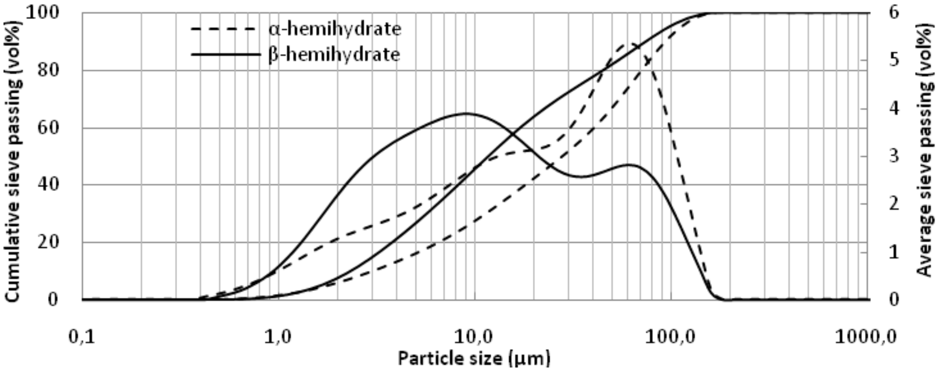

Figure 1: Particle size distribution of two hemihydrates.

Although the formation of dihydrate is endothermic the total hydration is exothermic because of the large heat released during the hemihydrate dissolution. The dihydrate precipitates from the solution quickly due to its lower solubility (2.62 g/l) than that of hemihydrate (8.72 g/l for β-hemihydrate) /1/. The generated gypsum experiences a continuous change due to nucleation and precipitation, the volume fraction reads /2/.

$$\varphi_g = \frac{m(v_h/v_w + w_0 v_n/v_w)}{v_h/v_w + w} \qquad (2)$$

Where φ_g is the volume fraction of gypsum, m hydration degree, v_h/v_w the specific volume ratio of hemihydrate/free water (0.36 for α- and 0.38 for β-hemihydrate), v_n/v_w the specific volume ratio of crystal water/free water (0.81 for α- and 0.71 for β-hemihydrate), w the water/hemihydrate ratio, and w_0 the water requirement for the hydration reaction (0.186 for both α- and β-hemihydrate).

The microstructure change during the hydration was investigated using ultrasonic method because the ultrasonic sound speed varies in different structures. Figure 2 shows the measured β-hemihydrate hydration results with the water/hemihydrate ratio of 0.65. Results show the system experienced first a stable period known as induction time and then a continuous change due to the formation of dihydrate until around nine minutes which indicates the completion of the hydration. The change of the ultrasonic speed clearly indicates the microstructure change during the hydration. It is also evident that the hydration speed varies during the hydration due to the formation and precipitation of gypsum. The measured hydration time is much shorter than value from /7/ with electrical resistance method. This probably can be explained by the difference between microstructure of used materials which also indicates its influence on hydration.

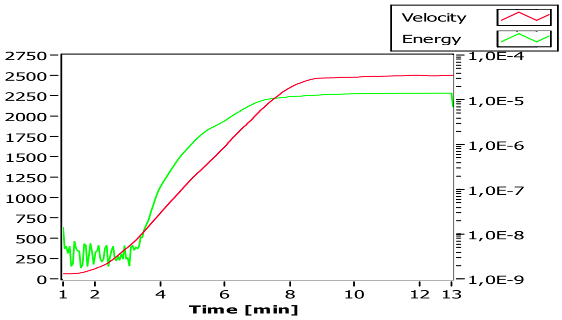

Figure 2: Hydration of β-hemihydrate measured with ultrasonic method (w/h=0.65) /5/.

Water influence on fresh behavior

Water plays a very important role in the hydration since it works not only as reactant but also as carrying liquid. From Eq. (1) it is evident that a same amount of water (w_0) is needed as reactant for the hydration reaction of both types of hemihydrates. However, an excess amount of water is necessary for the hydration to take place due to that all hemihydrate particles need to be covered with a water layer to promise the enough fluidity in induction period. Experiments with sprinkling methods /4/ show that a water amount of 33 wt.% of α-hemihydrate whereas 61 wt.% of β-hemihydrate is needed for the hydration reaction. This phenomenon is in line with the particle size results of the two hemihydrates that a higher water amount is needed for α-hemihydrate because of its higher surface area, which is confirmed by Hunger and Brouwers /5/ who pointed out that the water demand is related with the surface area, the resultant consistency, and the void volume of the hydrated structure.

Workability is used widely to describe the fresh properties of the cementitious materials like concrete and gypsum that is usually related to the parameters like fluidity, mobility, and compactability. Although many methods such as angles flow box test, flow table test, and slump test can be used to determine the workability, the spread flow test was used in the present study because it is especially suitable to measure the materials which have a collapsed slump. The spread flow tests were carried out by first filling the test material into the Hägermann cone and followed by lifting it to allow a free flow of the sample. The relative slump is calculated with equation (3) reads.

$$\Gamma_p = (d/d_0)^2 - 1 \tag{3}$$

Where d_0 is the base diameter of the Hägermann cone (d_0 = 100 mm), d is the mean value of the two perpendicular diameters measured from the spread sample.

Figure 3 shows the water influence on the gypsum workability with β-hemihydrate. Results show obviously the relative slump flow increases linearly with the water /hemihydrate ratio. The intersection of the trend line with the vertical axis (β_p) shows in this condition the slump is zero which indicates the minim water/hemihydrate should be 0.55 to promise a fluid gypsum plaster which is in line with the sprinkling method result. The deformation coefficient (E_p, the slope of the trend line) indicates the sensitivity of the tested materials to the water on the workability. A deformation coefficient of 0.062 for cement (CEM Ш/B 425) /3/ is given which is bigger than that of β-hemihydrate (0.053) in the present study which indicates the water has a bigger influence on the flow ability of the gypsum plaster which is probably due to its smaller surface area than that of the mentioned cement.

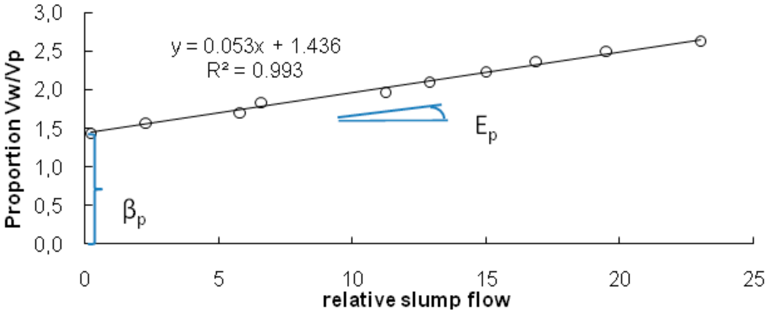

Figure 3: Result of spread flow test.

The microstructure development of gypsum is strongly related to the setting in hydration. Although method like X-ray diffraction can test both the dissolution of hemihydrate and the formation of dihydrate during hydration, knife cut closure and needle penetration depth methods are used widely to measure the setting because they are quick and easy to perform by only determining the formation of dihydrate. Setting is strongly related to the water amount which influences dissolution of the hemihydrate and precipitation of the gypsum. The influence of water on setting time is shown in Figure 4 with β-hemihydrate measured with knife cut method. It is evident that the setting time increases with water as a function of second order which indicates the stronger influence of water on setting time than that of flow ability. In gypsum plasterboard production, a fixed setting time is required to promise unified physical and mechanical properties. Fine dihydrate is usually used to accelerate the hydration to the desired setting time by changing the nucleation rates of generated dihydrate.

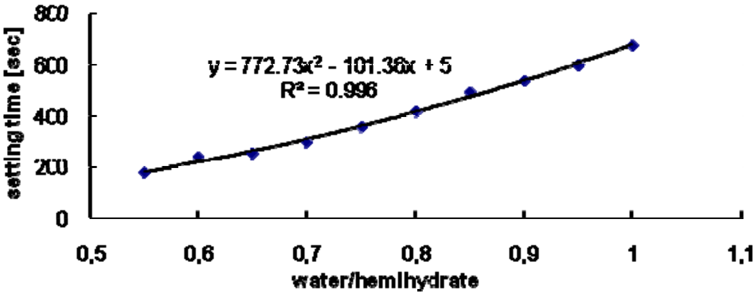

Figure 4: Influence of water on setting time of gypsum.

Water influence on void fraction

The void fraction is composed of two parts shown as equation (4) /2/. The first part is caused by the volume contraction during hydration because of the conversion of hemihydrate to dihydrate via the solution phase. This volume shrinkage increases linearly with the hydration degree which is influenced by water and the hemihydrate property. The second part is caused by the evacuation of excess water after hydration. The resulting total porosity reads

$$\varphi_p = \varphi_s + \varphi_w = \frac{\mathrm{m}(1 - v_n / v_w) w_0}{v_h / v_w + \mathrm{w}} + \frac{w - m w_0}{v_h / v_w + \mathrm{w}} = \frac{w - m\, w_0 v_n / v_w}{v_h / v_w + w} \qquad (4)$$

Where φ_p and is the total volume fraction, φ_s the volume fraction due to structure shrinkage during hydration, and φ_w volume fraction of evacuation of excess water.
Substituting the values of α-hemihydrate into equation (4) for full hydration an expression of the void fraction is obtained which is the same as Schiller /9/, who proposed this equation also assuming the volume keeps constant during hydration. An expression is obtained to describe the void fraction of gypsum generated with β-hemihydrate by substituting the values of β-hemihydrate, reading.

$$\varphi_p = \frac{w - 0.13m}{\mathrm{w} + 0.38} \qquad (5)$$

Sattler and Bruckner /8/ also proposed an expression of the void fraction of gypsum from β-hemihydrate shown as equation (6). However, this equation is wrongly proposed based on the volume after hydration is composed of the gypsum and the excess water without considering the void fraction caused by structure shrinkage during hydration.

$$\varphi_p = \frac{w - w_0}{(1 + w_0)/\rho_h + w - w_0} \tag{6}$$

Where ρ_h (g/cm^3) is the density of hemihydrate.

The influence of water on void fraction is studied by experiments and the proposed model is verified by experimental results shown in Figure 5 using β-hemihydrate in full hydration. Results clearly show the void fraction increases with the increase of water. The perfect agreement between the model value from equation (5) and the experimental data shows clearly the validity of the proposed model.

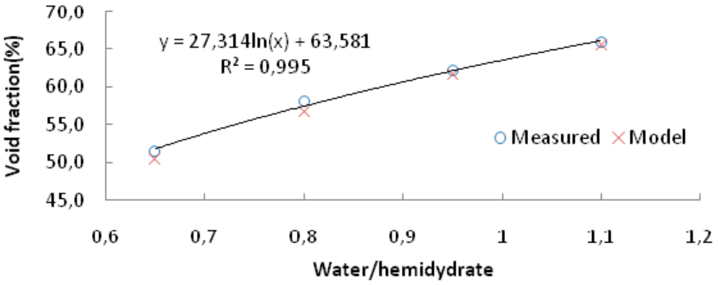

Figure 5: Results of the influence of water on void fraction of gypsum.

Conclusion

The present paper addresses the gypsum hydration study with the theoretical and experimental method. The microstructure of gypsum changes during the hydration reaction. The hydration speed changes during the hydration reaction due to the consumption of hemihydrate and formation of dihydrate.

1. Ultrasonic results indicate gypsum hydration reaction consists of two stages: the dissolution of hemihydrate in the first stage and the nucleation and precipitation of dihydrate in the second stage.
2. Gypsum hydration is strongly influenced by water amount. Spread flow test is suitable to determine the water demand for gypsum hydration. An excess of water is needed for good workability for the gypsum plasterboard production but a longer setting time is caused due to the high water amount.
3. Void fraction of the gypsum is caused by the volume shrinkage during hydration and the evacuation of the excess water. A model is proposed to describe the void fraction of gypsum and experimental results show its validity.

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Authors

Q.L. Yu (M.Sc), H.J.H. Brouwers (Prof. Dr. Ir.), and A.C.J. de Korte (Ir.). Department of Construction Management and Engineering, Faculty of Engineering Technology, University of Twente, P. O. Box 217, 7500 AE Enschede, The Netherlands.