Gypsum: an investigation of microstructure and mechanical properties

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Abstract
This article addresses the microstructure and mechanical properties of a β-hemihydrate produced gypsum from a combined study of hydration and dehydration. A thin layer of adsorbed water molecules around the particles is necessary to assure the fluidity of the hydrating system and the thickness of this water layer is derived using the spread-flow test. The shape factor of the investigated hemihydrate is derived from the spread-flow test. The mechanical property of the generated gypsum is investigated and the influence of water content is discussed. The dehydration of gypsum is studied by both thermo gravimetric analysis and heating the samples in a ventilated oven. A model is proposed to describe the microstructure change beyond dehydration and experimental results show its validity. The mechanical property of the gypsum beyond dehydration is presented as well.

1. Introduction

Gypsum ($CaSO_4{\cdot}2H_2O$, also as dihydrate) plaster is one of the earliest building materials elaborated by mankind, and gypsum plasterboard is used widely because of its easy fabrication, environmental friendliness, fire resistance, and aesthetics etc. Taking Europe as an example, there are 160 gypsum quarries and the number of employees is over 85.000 [1]. The annual world gypsum production in 2007 is over 250 million ton [2].

The hydration and dehydration of gypsum has been investigated intensively so far, whereas the emphasis is mainly on α-hemihydrate. Although great achievement has already been obtained, topics like the hydration induced properties and the problems caused by dehydration still needs further investigation, especially the behaviour of the β-hemihydrate and gypsum produced from it is still poorly understood. This article focuses on the role of water on the properties of gypsum produced from a β-hemihydrate due to its combined effect on both hydration and dehydration. The microstructure and mechanical properties of the gypsum beyond hydration and dehydration is investigated.

2. The water demand of β-hemihydrate

The determination of water demand of fine powders used in building materials such as concrete and gypsum is of vital importance for its mix design. Workability is used widely to describe the properties of concrete or gypsum in fresh state and it is related to the parameters like fluidity, mobility, and compactability. To assure the hydrating system is fluid, a thin layer of adsorbed water molecules around the particles is necessary [3].

Although many methods like angles flow box test, flow table test, or slump test can be used to determine the workability, the spread flow test was deployed here because it is especially suitable to measure the materials which have a collapsed slump [4]. A trend line can be fitted through the plotted values based on the spread flow test results, reads,

$$\frac{V_w}{V_h} = E_h \Gamma_h + \beta_h \tag{1}$$

Here Γ_h is the relative slump of the hydrating system and a detailed calculation can be found in [5], E_h is the deformation coefficient of the β-hemihydrate, β_h is the water/hemihydrate (vol. %) for Γ_h is zero, and V_w and V_h is the volume of water and hemihydrate, respectively.

The water demand (β_h) and the deformation coefficient (E_h) of the β-hemihydrate were already discussed in [5]. Here the emphasis is focused on the thin layer of adsorbed water molecules around the particles to assure the fluidity of the hydrating system. Brouwers and Radix [6] reported that the thickness of this layer is related to the deformation coefficient and the surface area of the used material, which was later confirmed by [3], reads,

$$E_h = \delta_{Blaine} \cdot a_{Blaine} \cdot \rho_h = \delta \cdot \xi \cdot a_{sphere} \cdot \rho_h \tag{2}$$

Here δ is water layer thickness (cm), a is specific surface area (cm^2/g), S is specific surface area (volume based, cm^2/cm^3), ρ_h is the density of the β-hemihydrate (g/cm^3), ξ is the shape factor and a_{sphere} the surface computed using the PSD and assuming spheres and subscript Blaine and sphere is the value measured according to Blaine method and PSD method, respectively.

In the present study, using a a_{Blaine} value of 3025 cm^2/g [7] and a ρ_h value of 2.32 g/cm^3, a δ_{Blaine} value of 66.8 nm is obtained, which is in line with [6] who reported a δ_{Blaine} value of 44.6 nm for CEM Ш/B 42.5 N LH/HS. Furthermore this is also confirmed by Marquardt [8] who reported a δ value of 150 nm with a different test, which was discussed in [3].

A linear relation was reported [3] between the specific surface area from Blaine method and computed specific surface area from PSD method, given by,

$$\xi \cdot a_{sphere} = 1.7 \cdot a_{Blaine} \tag{3}$$

Substituting the surface areas yields ξ = 1.16, which is in the same range as reported for α-hemihydrate [3].

3. Mechanical properties

The hardened gypsum is not a compact solid due to its high void fraction. Lewry and Williamson [9] reported that the gypsum strength develops during setting via a three-stage process: first a development of an interlocking matrix of dihydrate needles, then a relief of internal stress due to the build-up of pressure as needles, and final a strength increase during the removal of the excess water. One can see that the strength is related to the produced gypsum crystals and the bond between them. Some studies [10, 11, 13] were carried out on the influence of the void fraction on the mechanical properties of the gypsum. However, the relation between them is still not clear, which is therefore investigated here.

The strength tests were performed according to [12]. The preparation of the test samples strictly follows [12] since Coquard et al. [13] reported that the sample size has an obvious influence on the test results. The flexural strength was measured with the three-point bending method. The compressive strength was determined by using the broken part of the specimen from the flexural strength test.

The influence of water on the strength of gypsum was investigated by testing samples with different w_0/h_0 range from 0.65 to 1.10. The results are shown in Fig. 1. It is evident that the strength decreases with the increase of the void fraction. These findings can be explained by the bond between the crystals. The void fraction of the generated gypsum increases when the water amount increases [3] which in turn leads to a weaker bond between the gypsum crystals. This finally results in a decreased strength.

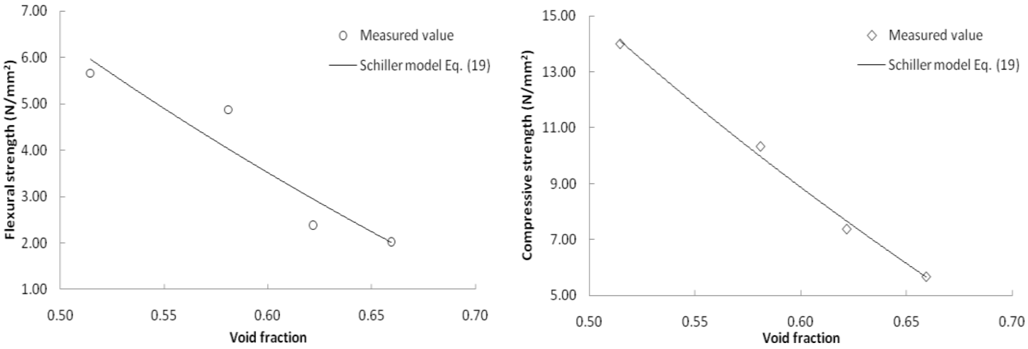

Figure 1: Mechanical properties of the gypsum versus the void fraction.

Results show that both flexural and compressive strength decrease as the increase of water content according to a logarithmic law, which is in line with Schiller [14] who proposed a model to describe the relation between the void fraction and the strength of the gypsum based on the same rule. A critical void fraction value of 0.76 of the gypsum is obtained here. This value means that gypsum will lose its strength at this void fraction, which is also confirmed by Schiller [14] who reported a critical void fraction value of 0.79. However, as discussed in Coquard et al. [13], the size of the samples and test methods affect the results greatly. Therefore we only can conclude the logarithmic model gives the optimum results under the present conditions and further study is still necessary for a comprehensive understanding.

4. Dehydration of gypsum

Gypsum contains about 21% of chemically combined water by weight, which will dissociate from the crystal lattice and vaporize when gypsum is exposed to fire or heated. A common understanding is that gypsum undergoes two endothermic decomposition reactions at two different temperature ranges.

$$CaSO_4 \cdot 2H_2O + heat \rightarrow CaSO_4 \cdot 0.5H_2O + 1.5H_2O \tag{4}$$

$$CaSO_4 \cdot 0.5H_2O + heat \rightarrow CaSO_4 + 0.5H_2O \tag{5}$$

However, until now available research findings vary with each other greatly. The evident difference raises the question whether the dehydration mechanism is already clear or not. Therefore, the dehydration of gypsum is investigated here with both thermo gravimetric analysis (TGA) and heating the samples in a ventilated oven. The used TGA set-up (Perkin Elmer TGA 7) has a test temperature range of 20-1000 °C with a scanning rate between 0.1-200 °C/min and a test mass capacity of 1300 mg under the atmosphere of Nitrogen. In the present study, a fixed scanning rate of 10 °C/min was used and the samples were heated until 900 °C since anhydrite II converts to anhydrite I above 1180 °C [14], which indicates anhydrite remains stable in this temperature range. The mass of the test sample was chosen between 30-50 mg here. The test samples were taken from the prepared gypsum prisms. The gypsum prisms were heated in the oven with a manual temperature adjustment to 55 °C, 80 °C, 120 °C, 190 °C, and 220 °C respectively and the mass was measured continuously to ensure that mass reaches to constant at every step.

The mass loss measured with TGA is shown in Fig. 2, which shows that the sample starts to lose weight at around 80 °C and the mass becomes constant again at around 220 °C which is in line with the results from oven test [3] and then from about 620 °C it starts to lose weight again until around 800 °C. This is confirmed by [16] and [17]. However, here only one obvious inflection point in the derivative weight loss curve during the first dehydration step is obtained which occurs at 167 °C as shown in Fig. 10, whereas in [17] a two-inflection point finding was reported.

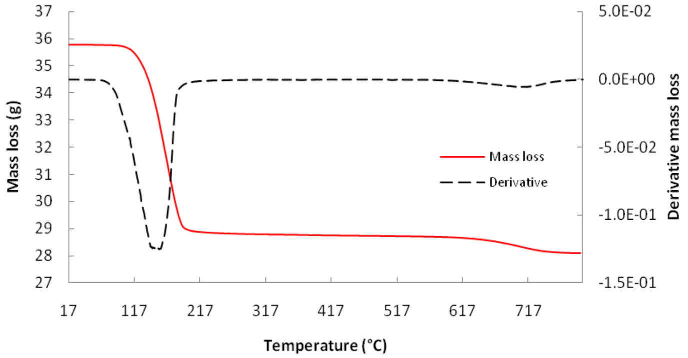

Figure 2: Mass loss measured using TGA.

As illustrated in Eqs. (4) and (5), anhydrite is generated after the total release of chemically combined water from gypsum. Therefore, the volume composition of the fully dehydrated system consists of only anhydrite and void fraction, i.e. air. During the dehydration the mole amount of $CaSO_4$ remains constant, so the following expression is obtained,

$$\frac{\varphi_{ah}}{\omega_{ah}} = \frac{\varphi_g}{\omega_g} \tag{6}$$

Here ω is specific molar volume (cm^3/mol), φ is volume fraction, and subscript ah and g mean anhydrite and gypsum, respectively.

Therefore the void fraction of the generated anhydrite is derived as following,

$$\varphi_{v,ah} = 1-\varphi_{ah} = 1-\frac{\varphi_g}{\omega_g}\times\omega_{ah} = 1-(1-\varphi_{v,g})\times\frac{\omega_{ah}}{\omega_g} = \frac{0.01+w_0/h_0}{0.38+w_0/h_0} \tag{7}$$

Here w_0/h_0 is initial water/hemihydrate ratio (by mass) for the gypsum production, and subscript v,ah and v,g is the void fraction of anhydrite and gypsum, respectively.

In the present study, experiments were carried out with different w_0/h_0 to study the void fraction of the system beyond dehydration. The results are shown in Fig. 3. The perfect agreement between the derived model (Eq. (7)) and the measured value indicates the validity of this model. The results also show that the assumption that the total volume of the system remains constant during the dehydration is correct.

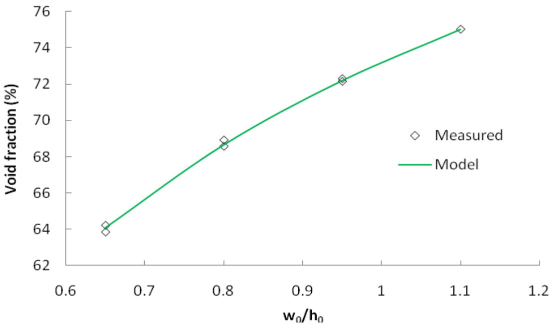

Figure 3: The void fraction of dehydrated system versus w_0/h_0.

The chemically combined water is released from the gypsum during the dehydration which leads to an interactive change between the crystals of the remaining materials. This study investigated the influence of the water release on the strength induced by the dehydration. First the gypsum prisms were heated in the ventilated oven under 220 °C until the mass is constant. Then the mechanical property of the samples was determined after cooling down to room temperature.

The strength loss of the samples produced with different w_0/h_0 after dehydration is shown in Fig. 4. Results show that the strength of the gypsum with a higher void fraction decreased more than that of gypsum with a lower void fraction. This indicates evidently that the matrix of the gypsum with a higher void fraction becomes weaker compared to the gypsum with a lower void fraction. Also the flexural strength of the gypsum in different water content conditions decreased more compared to the compressive strength loss. These findings show that the strength of the gypsum is built based on the bond between the crystals and the water release of the gypsum has a higher influence on the gypsum with a higher void fraction.

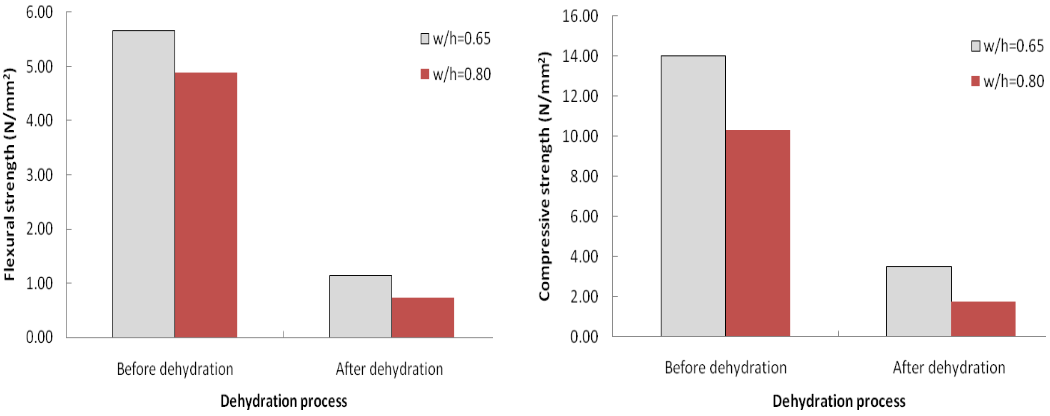

Figure 4: Mechanical properties change beyond dehydration.

5. Conclusions

This article addresses the microstructure and mechanical properties of the gypsum produced from the hydration of β-hemihydrate and water. The investigation was carried out from a combined study of hydration and dehydration process since hydration reaction decides the microstructure and mechanical property of gypsum and dehydration reaction changes them greatly.

1. The water demand of the hemihydrate is of vital importance to ensure the hydration reaction. A thickness of a thin water layer of adsorbed water molecules around the particles is found by the spread flow test. A shape factor of the investigated β-hemihydrate is derived by applying a model from [6].
2. The mechanical properties of the generated gypsum are dependent greatly on the void fraction (water content related). A relation between the strength and the void fraction of the gypsum according to a logarithmic law is found. A critical void fraction value of 0.76 of the gypsum is found. This value means that gypsum will lose its strength at this void fraction.
3. Experimental results show that the gypsum starts to lose chemically combined water at around 80 °C, and only one inflection point is found in the present study. A void fraction of the dehydrated system is proposed and experiments show its validity.
4. The strength of gypsum decreases greatly beyond dehydration. Results indicate that the matrix of the gypsum with a higher void fraction becomes weaker compared to the gypsum with a lower void fraction.

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