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Determination of a partial phase composition in calcined gypsum by calorimetric analysis of hydration kinetics

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Abstract A calorimetric method for the determination of a partial phase composition in calcined gypsum is presented. The method is based on the separation of the reaction heat of the transformation of β-anhydrite III to β-hemihydrate from the main hydration reaction transforming β-anhydrite III to dihydrate. Using the known hydration heats of β-anhydrite III to dihydrate and β-hemihydrate to dihydrate, the content of β-calcium sulfate anhydrite III and β-calcium sulfate hemihydrate as well as the amount of non-hydrating parts in gypsum can be determined. Practical application of the method is illustrated on three industrial products.

Keywords Gypsum · Calcium sulfate anhydrite III · β-Calcium sulfate hemihydrate · Heat flow calorimeter

Introduction

Calcined gypsum is produced during a thermal process in which most of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$) is transformed to calcium sulfate hemihydrate ($CaSO_4{\cdot}½\,H_2O$), while a part of it is transformed to calcium sulfate anhydrite ($CaSO_4$). The process is described by the endothermic reactions

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot {}^1\!/\!_2H_2O + 1{}^1\!/\!_2H_2O \quad (1)$$

and

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O \quad (2)$$

Two different processes of the dehydration of calcium sulfate dihydrate are commonly employed. One is the dry method in which β-gypsum is produced by the calcination of gypsum at the atmospheric pressure and temperatures between 120 and 180 °C [1]; the product is known as stucco, kettle stucco, plaster, plaster of Paris, or calcined gypsum. The other one is the wet method carried out under pressure at temperatures above 100 °C in a water-vapor saturated atmosphere, resulting in α-gypsum [1]. Although β-gypsum has a significantly lower strength than α-gypsum, it is usually preferred for industrial purposes because the technology of its production is much simpler and more economical [1, 2]. From the chemical point of view, both these types of calcined gypsum are similar. However, they differ in the size of crystals and specific surface and have a different content of crystal water [3–9]. In this article, we will consider only β-gypsum because it is an ecologic building material and its production consumes less energy in comparison with other binders such as cement or lime.

In the atmospheric air under the standard conditions calcined gypsum consists of calcium sulfate β-hemihydrate, β-calcium sulfate anhydrite III, calcium sulfate anhydrite II, and various impurities originating mainly from raw materials. The presence of anhydrite in calcined gypsum is caused by the technology of gypsum production, in particular, by the method of heating and by the chosen temperature of the calcination process [1]. In Table 1, we provide more details on the calcium sulfate anhydrite modifications.

During the hydration of β-phases of gypsum sulfates in calcined gypsum, β-anhydrite III changes to β-hemihydrate

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Table 1 Modifications of calcium sulfate anhydrite [1]

Modification	Anhydrite III (A III)	Anhydrite II (A II; γ)	Anhydrite I (A I)
Crystal structure	Tetragonal	Rhombic	Cubic
Thermal stability	<40 °C	40–1180 °C	>1180 °C
Form	β-A III	A II-s (slowly soluble)	
	β-A III′	A II-u (insoluble)	
	α-A III	A II-E (Estrich gypsum)	
Production temperature	β-A III and β-A III: 290 °C	300–900 °C	Not produced commercially
		A II-s: <500 °C	
		A II-u: 500–700 °C	
	α-A III: 110 °C	A II-E: >700 °C	

with a fast evolution of the hydration heat. This occurs almost immediately after adding water according to the equation

$$CaSO_4 + {}^{1}\!/_{2}H_2O \rightarrow CaSO_4 \cdot {}^{1}\!/_{2}H_2O \qquad (3)$$

The hydration of β-anhydrite III is completed within several minutes and, subsequently, the hydration of β-hemihydrate to dihydrate begins,

$$CaSO_4 \cdot {}^{1}\!/_{2}H_2O + {}^{1}\!/_{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O, \qquad (4)$$

taking up to a thousand seconds. Using Q_{HH} to denote the hydration heat of reaction (4) and Q_A to denote the hydration heat of the β-anhydrite III–dihydrate transformation, the hydration heat of reaction (3) becomes Q_A–Q_{HH}. The latter heat increases the absolute value of the total hydration heat of gypsum. On the other hand, the non-hydrating calcium sulfates (anhydrite II or calcium sulfate dihydrate, the latter being usually absent from calcined gypsum) and impurities in gypsum reduce the value of the total hydration heat because they do not take part in hydration reactions.

Calorimetric measurements are commonly used to investigate gypsum both in scientific laboratories and in industry. Folek and Kowol [10] performed a calorimetric analysis of various calcium sulfate phases during the gypsum hydration. Kuzel [5] presented comprehensive results on the hydration heats of pure α-calcium sulfates. Dantas et al. [11] used the temperature modulated differential scanning calorimetry to identify gypsum phases after the calcination of $CaSO_4{\cdot}2H_2O$. Rahhal et al. [12] performed calorimetric studies of Portland cement with a gypsum addition and found that the addition of gypsum to Portland cement resulted in a larger specific heat of the hydration. Tydlitát et al. [13] analyzed the effects of the calorimeter type and the use of plasticizers and hydrophobizers on the measured hydration heat evolution of flue gas desulfurization (FGD) gypsum. Fischer [14], Fietsch and Ramdohr [15], and Gerard [16] applied the results on the hydration heat evolution to monitor gypsum manufacturing. In Table 2, we provide an overview of the measured hydration heats of phases in the system $CaSO_4{\cdot}H_2O$ reported since 1924 [5, 17–21]. The units J mol^{-1} used for the hydration heats are independent of the molecular mass of the pure $CaSO_4{\cdot}H_2O$ phase. Since many authors present the hydration heats in J g^{-1}, we also provide the data in Table 2 relative to the masses of $CaSO_4{\cdot}H_2O$ phases. The discrepancies in literature data on the hydration heat found by Nowak et al. [22] may be attributed to different units in their presentation.

In this article, a method for the separation of the hydration heat of β-calcium sulfate anhydrite III from the hydration heat of β-calcium sulfate hemihydrate during the hydration heat evolution in calcined gypsum is presented. Using a measured hydration heat of gypsum and the known hydration heats of both components, the method allows one to determine the amounts of the β-anhydrite III, the β-calcium sulfate hemihydrate, and the non-hydrating components in gypsum.

Experimental

The calorimetric measurements were performed with an isothermal heat flow calorimeter KC 01. It made possible isothermal measurements of the hydration heat power as a function of time at the laboratory temperature 25 ± 1 °C. The construction of the calorimeter was described in [13, 23], so we will not go into details here. In order to collect experimental data on the measured voltage that is proportional to the hydration heat power, we used a datalogger MS 2 (Comet). The calibration of the calorimeter was based on the Joule heat principle, using a resistor with the precisely known resistance of 9.99 kΩ placed into a reaction vessel and powered by a controlled DC power supply.

Table 2 The hydration heats of the phases in the system $CaSO_4 \cdot H_2O$ in different units

Phase		Hydration heat				Reference
	g mol^{-1}	J mol^{-1}	J g_{CaSO4}^{-1}	J g_{phase} $^{-1}$	J $gCaSo_4 \cdot 2H_2O^{-1}$	
$CaSO_4 \cdot 2H_2O$	172.1723					
α-Hemihydrate (techn.)	145.1493	18338		126.34	106.51	[17]
α-Hemihydrate	145.1493	20920		144.13	121.51	[18]
α-Hemihydrate	145.1493	17166		118.26	99.70	[19]
α-Hemihydrate	145.1493	15910		109.61	92.41	[20]
α-Hemihydrate $CaSO_4 \cdot 0.53H_2O$	145.6897	17709		121.55	102.86	[5]
α-Hemihydrate $CaSO_4 \cdot 0.62H_2O$	147.3111	16981		115.27	98.63	[5]
β-Hemihydrate (techn.)	145.1493	19430		133.86	112.85	[17]
β-Hemihydrate	145.1493	19260		132.69	111.86	[19]
α-AIII	136.1416	27500	202.00	202.00	159.72	[20]
α-AIII $CaSO_4 \cdot 0.03H_2O \rightarrow CaSO_4 \cdot 2H_2O$	136.6821	28001		204.86	162.63	[5]
α-AIII $CaSO_4 \cdot 0.03H_2O \rightarrow CaSO_4 \cdot 0.53H_2O$	136.6821	10992		80.42		[5]
α-AIII $CaSO_4 \cdot 0.03H_2O \rightarrow CaSO_4 \cdot 0.62H_2O$	136.6821	11000		80.48		[5]
β-AIII	136.1416	30187	221.73	221.73	175.33	[19]
β-AIII	136.1416	29270	215.00	215.00	170.00	[21]

Results and discussion

Hydration heats

In Fig. 1, we show an example of the evolution of the original hydration heat power measured for FGD gypsum (produced by the calcination of FGD calcium sulfate dihydrate). The transformation of β-anhydrite III to hemihydrate corresponds to the first peak in the total hydration heat evolution, while the second peak is associated with the transformation of hemihydrate to dihydrate.

For the sake of illustration, in Fig. 2 we show the evolution of the hydration of impure anhydrite III prepared by the calcination of FGD gypsum for 2 h at 200 °C. We observe that a tall first peak associated with the transformation of anhydrite III to hemihydrate occurs in this case, followed by a much smaller peak associated with the hydration of hemihydrate to dihydrate.

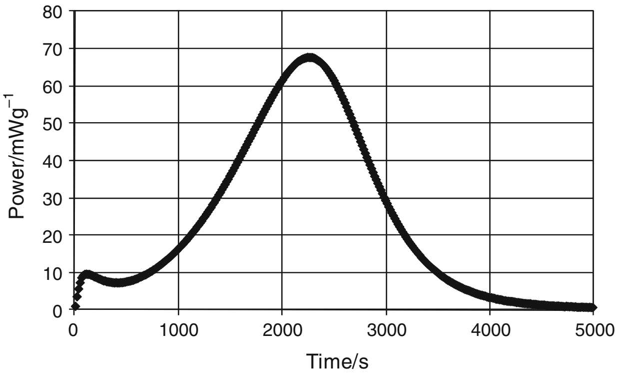

Fig. 1 The time evolution of the hydration power of calcined FGD gypsum exhibiting two peaks

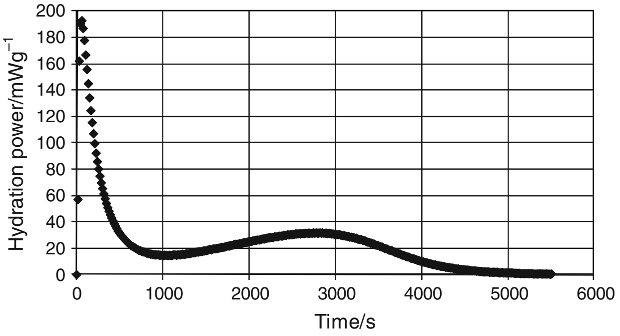

Fig. 2 The time evolution of hydration of impure β-anhydrite III to dihydrate

The areas under the hydration power peaks (see Fig. 2) coincide with the heats of hydration associated with the peaks: the first peak's area corresponds to the hydration heat, h_A, of the β-anhydrite III–β-hemihydrate transformation, whereas the second peak's area to the sum of the hydration heat, h_{HH}, of the β-hemihydrate–dihydrate transformation and the hydration heat, h_{HHA}, of the hemihydrate which originates from the hydration of anhydrite described by Eq. 3. These heats are fundamental quantities necessary for our method of the determination of the content of β-anhydrite III, β-calcium sulfate hemihydrate, and non-hydrating remains in calcined gypsum.

The total hydration heat of calcined gypsum, h_{tot} (J g^{-1} of calcined gypsum), determined in a standard calorimetric measurement may be expressed as

$$h_{\mathrm{tot}} = h_{\mathrm{A}} + h_{\mathrm{HH}} + h_{\mathrm{HHA}}, \tag{5}$$

where h_{HHA} may be calculated from the formula

$$h_{\mathrm{HHA}} = \frac{Q_{\mathrm{HH}}}{Q_{\mathrm{A}} - Q_{\mathrm{HH}}} h_{\mathrm{A}} \tag{6}$$

Here Q_{A} (J mol^{-1} of anhydrite) is the reference hydration heat of the β-anhydrite III–dihydrate transformation and Q_{HH} is the reference hydration heat of the β-hemihydrate–dihydrate transformation.

Reference data on hydration heats

The accuracy of our method is, to a substantial extent, determined by the accuracy of the reference hydration heats. In Table 2 we provide the hydration heats reported since 1924 both in J mol^{-1} and J g^{-1} of the phase in the reaction equation. From Table 2 one may notice the dependence of the values in J g^{-1} on the relevant $CaSO_4 \cdot H_2O$ phase. Taking the average of the relevant data from Table 2, we obtained the values of the reference hydrations heats Q_{A} (the β-anhydrite III–dihydrate transformation) and Q_{HH} (the β-hemihydrate–dihydrate transformation) that in turn yielded the hydration heat, Q_{A}–Q_{HH}, of the β-anhydrite III–β-hemihydrate transformation (see Table 3).

Separation of the hydration heats

Figure 1 shows the time dependence of the total hydration power of calcined gypsum from which total hydration heat h_{tot} of calcined gypsum may be obtained by integration. According to Eq. 5, it may be expressed as a sum of two contributions, h_{A} and $h_{\mathrm{HH}} + h_{\mathrm{HHA}}$. In order to separate these two contributions, we shall assume that the following is true:

(i) The heat power of the β-hemihydrate hydration smoothly increases with time before it reaches its maximum and is equal to 0 at the initial time $t = 0$.
(ii) The hydration reaction of anhydrite is completed after the time period equal to 10 t_1, where t_1 is the maximum position of the first hydration power peak.

Table 3 The reference hydration heats

Hydration reaction	Reference hydration heat (mean value) (J mol^{-1})	Uncertainty (%)	Reference
β-AIII to HH	Q_{A}–Q_{HH} = 10383.5	8.3	Calculated
β-HH to DH	Q_{HH} = 19345.0	0.9	[17, 19]
AIII to DH	Q_{A} = 29728.5	8.0	[19, 21]

The data represent the mean measured values from Table2

Now, let us consider the monotonous part of the curve from Fig. 3 that lies between the time at which the hydration of β-anhydrite ends (about 920 s in Fig. 1) and the time at which the inflexion point occurs before the second peak maximum (about 1650 s in Fig. 1). This monotonous part of the curve represents the hydration reaction of β-hemihydrate and is shown in Fig. 3. We approximate it by a polynomial of order 5 or less, taking into account assumption (i), i.e., by a polynomial of the form $(a_1 t + \ldots + a_n t^n)$ with $n \leq 5$ (see Figs. 4, 5). As a result, we may separate the peak corresponding to the β-anhydrite III–hemihydrate hydration power from the total hydration power curve (see Fig. 6). Evaluating the area of the separated peak (the area between the measured

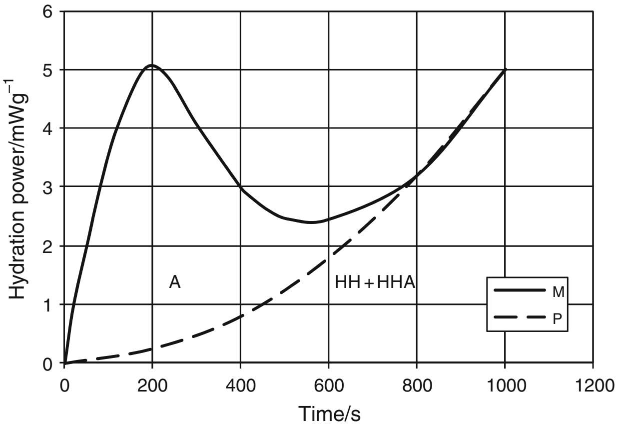

Fig. 3 The method for the separation of the hydration heats of β-calcium sulfate anhydrite III and β-hemihydrate (an illustration). Here M is a measured hydration heat power of gypsum containing anhydrite III (denoted by A) and β-hemihydrate (denoted HH+HHA), while P is a computed limit between the hydration power of anhydrite III and β-hemihydrate. HH denotes the hemihydrate contained in gypsum and HHA the hemihydrate occurring by the hydration of anhydrite

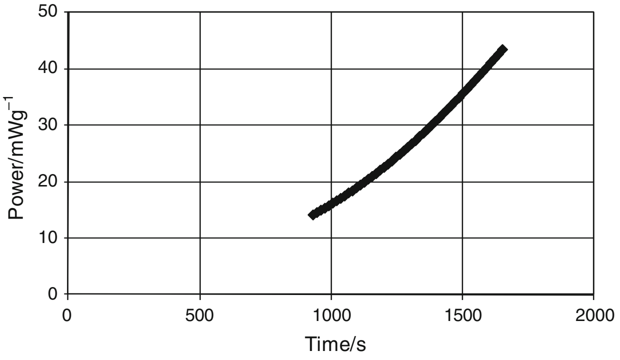

Fig. 4 The polynomial of the fifth order that very accurately ($R^2 = 0999986$) approximates the part of the hydration power between the point where the hydration of anhydrite III to hemihydrate is finished (920 s) and the inflexion point before the second peak (1650 s), see Fig. 1

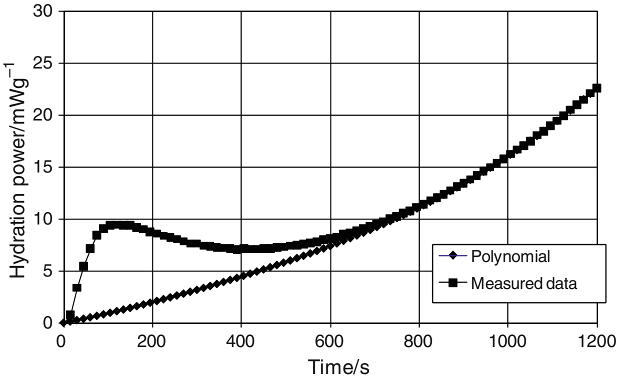

Fig. 5 The initial part of the hydration reaction heat power of calcined FGD gypsum (see Fig. 1). The curve "polynomial" represents the polynomial approximation of the hydration reaction power of hemihydrates

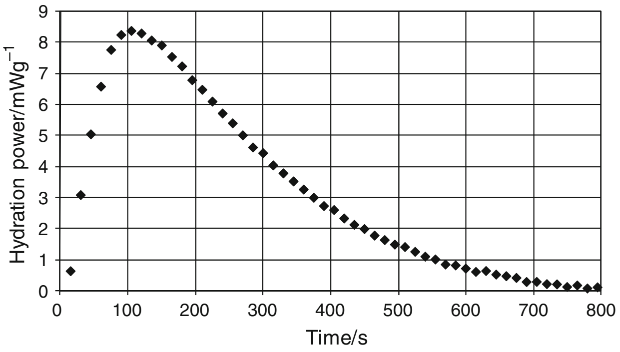

Fig. 6 The time evolution of hydration of β-anhydrite III to hemihydrate as separated from the dependence shown in Fig. 1

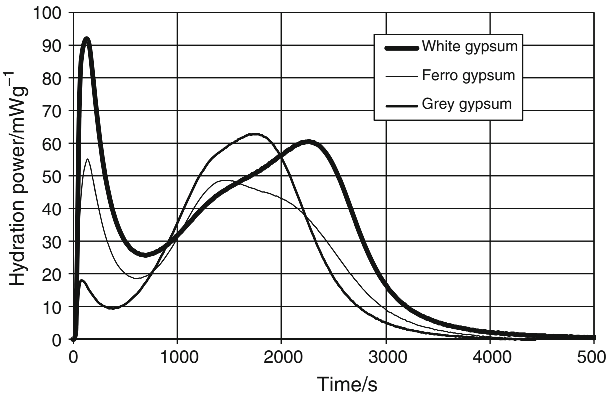

Fig. 7 The time dependences of the hydration power for three industrial gypsum products

data and the polynomial from Fig. 5), one gets the hydration heat h_A.

Once h_A is determined, the remaining hydration heat $h_{HH} + h_{HHA}$ may be readily obtained from Eq. 5 because h_{tot} is already known. Applying this method, we obtained values of the heats h_{tot}, $h_{HH} + h_{HHA}$, and h_A for three industrial types of gypsum (see Fig. 7; Table 4).

Mass evaluation

It remains to use our above results on the hydration heats and evaluate the amounts of β-anhydrite III and β-hemihydrate in gypsum. The amount of β-anhydrite III, m_A, is defined as the β-anhydrite mass in grams per 1 g of gypsum. It may be calculated as the ratio of the part of the total hydration heat of gypsum associated with the reaction of β-anhydrite to dihydrate to the respective reference hydration heat,

$$m_A = \frac{h_A + h_{HHA}}{Q_A} M(A) = \frac{h_A}{Q_A - Q_{HH}} M(A), \tag{7}$$

where we used Eq. 6 and $M(A)$ stands for the molecular weight of β-anhydrite. Similarly, the amount of the β-hemihydrate, m_{HH}, is defined as the β-hemihydrate mass in grams per 1 g of gypsum and may be obtained as

$$m_{HH} = \frac{h_{HH}}{Q_{HH}} M(\mathrm{HH}), \tag{8}$$

where M(HH) is the molecular mass of β-hemihydrate. Finally, the amount of non-hydrated parts in 1 g of gypsum, $m_{IM,}$ is

$$m_{IM} = 1 - m_A - m_{HH}. \tag{9}$$

Since we already evaluated the hydration heats h_A and h_{HH}, we may use Eqs. 7–9 to easily obtain the amounts m_A, m_{HH}, and m_{IM} of β-anhydrite III, β-hemihydrate, and impurities, respectively, in gypsum. The results are summarized in Table 4.

Notice that the content of non-hydrating impurities, m_{XRF}, as determined by the XRF analysis is much lower than the amount m_{IM} determined by the above-described method. This is, evidently, due to the occurrence of non-hydrating phase (stable calcium sulfate anhydrite II) in the product. At higher temperatures, metastable anhydrite III easily transforms to stable anhydrite II that hydrates very slowly in an irreversible process. This observation was

Table 4 The measured hydration heats and the content of phases and impurities in three industrial products

Product	h_{tot} (J $g_{product}^{-1}$)	h_A (J $g_{product}^{-1}$)	m_A (J $g_{product}^{-1}$)	m_{HH} (g_{phase} $g_{product}{}^{-1}$)	m_{IM} (g_{phase} $g_{product}{}^{-1}$)	m_{XRF} (g_{phase} $g_{product}{}^{-1}$)	m_{AII} (g_{phase} $g_{product}{}^{-1}$)
White stucco gypsum	136.26	25.70	0.337	0.470	0.193	0.017	0.176
Grey gypsum	98.00	4.00	0.052	0.649	0.298	0.102	0.193
Ferrogypsum	102.25	16.09	0.211	0.423	0.367	0.197	0.170

acknowledged, for example, by Kuzel [16] who prepared pure anhydrite III. In Table 4, the difference between m_{IM} and m_{XRF} are attributed to the content of anhydrite II, m_{AII}. As one may observe, the values of m_{AII} are for all three studied types of gypsum rather close to each other.

Conclusions

A method for the separation of different hydration reactions taking place during the hydration of calcined gypsum was proposed. The method can be used to determine the content of β-calcium sulfate anhydrite III that originates from specific features of the technology of the gypsum production. In particular, the method of heating and a chosen time-dependence of temperature of the calcination process are important. The presence of β-calcium sulfate anhydrite III in a mixture with β-calcium sulfate hemihydrate leads to a significant increase of the hydration heat of gypsum, which can affect the properties of hardened gypsum and, thus, the efficiency of its practical application.

The content of non-hydrating impurities that are commonly contained in calcined gypsum may be also determined using the proposed method, if the hydrations heats of β-calcium sulfate anhydrite III and β-calcium sulfate hemihydrate are known with a sufficient accuracy. The impurities are usually the main indicator of (and the main reason for) undesired worsening of mechanical properties of hardened gypsum. Therefore, the method may be conveniently applied both in research and in industry for a preliminary estimation of the quality of calcined gypsum to be used for a specific purpose.

The proposed calorimetric measurement and theoretical analysis enables one to obtain a partial phase composition of calcined gypsum by the determination of the content of β-hemihydrate and anhydrite III, the phases susceptible to hydration. However, it is not applicable to mixtures of α- and β-hemihydrates.

Gypsum materials that are stored for a long time may be partially hydrated and may, in a non-equilibrium state, contain also calcium sulfate dihydrate that increases the content of the non-hydrating material m_{IM}

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