Quality control of commercial plasters by thermogravimetry

J. Dweck[*], E.I.P. Lasota

Inorganic Process Department, School of Chemistry, Federal University of Rio de Janeiro, Bloco E do CT, Cidade Universitária, Rio de Janeiro, CEP 21949-900, Brazil

Abstract

Depending on the manufacturer, some 1 kg bags of commercial plaster of Paris have little holes in order to decrease their volume for storage. Because this exposes the plaster to the humidity of the air, there is a partial conversion of the plaster to calcium sulfate dihydrate, changing the original quality of the product. This work has, as its objective, the development of methods to estimate the contents of calcium sulfate hemihydrate, calcium sulfate dihydrate and inert components of the plaster by use of dynamic or isothermal thermogravimetry (TG). Using dynamic TG the different contents can be measured directly by one analysis, otherwise, they can be measured by the combined results of the two isothermal analyses, of the original sample, and of a modified sample obtained after total hydration and a drying step of the original one. In isothermal analysis dehydrations of both salts occur simultaneously and there are insufficient data to calculate the contents by only one analysis. The methods and the results obtained for the two types of plasters are shown and discussed, indicating that the analyzed samples have from 82 to 89 mass % of hemihydrate, a content from 5 to 10 mass % of the dihydrate and from 5 to 7 mass % of inerts. © 1998 Elsevier Science B.V.

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1. Introduction

Commercial plaster of Paris has calcium sulfate hemihydrate as its main compound ($CaSO_4 \cdot 1/2H_2O$), which is obtained by the partial dehydration of gypsum according to reaction R-1 [1]. When plaster is mixed with water, the inverse reaction occurs, during which the dihydrate is formed and, as a result of setting, the final product becomes rigid. Thus, it is possible to make solid bodies with different shapes for applications such as molds for ceramic slip casting, decorative objects and plates for civil construction, etc.

$$CaSO_4 \cdot 2H_2O \rightleftarrows CaSO_4 \cdot 1/2H_2O$$
$$+ 3/2H_2O \,(\text{mass loss} = 15.71\%) \qquad \text{(R-1)}$$
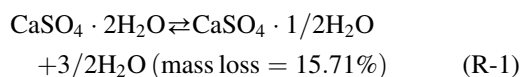
When purchasing commercial plaster, depending on the manufacturer the presence of holes in 1 kg plastic bag was observed. The holes were made so that the bags occupy less volume on storage. As a result, partial hydration by ambient storage humidity occurs and calcium sulfate dihydrate is formed, modifying the properties of the product and consequently, its quality.

The characterization and analysis of gypsum and plaster products by chemical or by thermal analysis are widely discussed in the literature [1,2–9]. Reaction (R-1) occurs at 34°C in dry air [1] and at higher temperatures, as the water ambient vapor pressure

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*Corresponding author. Tel.: +55 215903192; fax:+ 55 215904991; e-mail: dweck@ h2o.eq.ufrj.br

(p_w) increases. According to the equilibrium phase diagram of the system [10], when p_w<0.1013 MPa, the resulting plaster will be composed of the β hemi-hydrate. This can occur at temperatures lower than 100°C. If p_w>0.1013 MPa, α hemihydrate will be formed at temperatures higher than 100°C. The decomposition of both types of hemihydrate to anhydrite, occurs at higher temperatures than the respective gypsum decomposition, and can lead to anhydrite II at p_w>0.03039 MPa or to anhydrite III at p_w<0.03039 MPa, and then, at higher temperatures, to anhydrite II.

Duval [5] reports different thermogravimetric (TG) results for precipitated calcium sulfate dihydrate and for natural gypsum, when heated in open vessels at 3.5°C min^{-1}. The former is totally decomposed to hemihydrate up to 70°C. From this temperature to 80°C a small plateau is observed with no mass loss, and the last half molecule of water then disappears between 82°C and 105°C. On the other hand, the decomposition TG curve of natural gypsum begins at 62°C and ends at 190°C and gives no indication of discontinuity during dehydration.

Decomposition of the gypsum samples occurs at higher temperature ranges than plaster of paris or hemihydrate samples. For the former, in DTA curves obtained at higher heating rates, decomposition occurs from 100°C to about 300°C, with overlapped peaks of the two steps [3,6,7]. For the hemihydrate, even in open crucibles, the decomposition range is from about 60°C to 250°C [3,8], with an initial separate and broad peak of the decomposition of some existent dihydrate. By TG, using closed pans with pinholes, the hemi-hydrate loses weight even at temperatures as low as 50°C [9].

As can be seen, the system is quite complex, and the stability of the several phases depend on the tempera-ture and the ambient water vapor pressure to which the samples are effectively exposed. This explains why in thermal analyses of gypsum and its related com-pounds, the operating conditions, characteristics of the equipment, as well as the construction and the material of the crucible, have a direct influence on the resulting decomposition curves [11].

This work has as its objective the development of methods to estimate the contents of calcium sulfate hemihydrate, dihydrate and inert material of commer-cial samples of plaster of paris by dynamic and/or isothermal TG. The inert material represents the other additives present in the sample. Using dynamic TG the several contents are measured directly in one analysis. Using isothermal TG they are measured by combining the results of an isothermal analysis of the original sample, with that of a modified sample, obtained after total hydration and a drying step at 45°C of the original sample, to transform all the hemihydrated calcium sulfate into the dihydrate. The second run allows one to calculate the inert content and this is necessary because in the run of the original sample, the hydrated salts decompose simultaneously and there is insufficient data to calculate the content.

2. Experimental procedure

The analyses were performed in a microprocessor prototype for TG [12], which can analyze samples having laboratory scale masses with a sensitivity of 0.001 g, from ambient temperature to 1000°C, with variable heating rate and frequency of acquisition of data. The prototype uses a commercial digital balance, above which is assembled the heating chamber of a common laboratory furnace. A special mechanical device links the plate of the balance to a sample holder which is set in the heating chamber of the furnace.

Two commercial plasters, denoted as types A and B (for ethical reasons), were analyzed. Dynamic TG was performed at 5°C min^{-1} from ambient temperature using sample masses of about 2.5 g. Isothermal runs were performed at 250°C, 275°C and 300°C. For isothermal experiments, the prototype allows the introduction of the samples into the heating chamber at the desired temperature, avoiding the pre-heating step which occurs in most equipments before the isothermal conditions were attained.

3. Dynamic TG method

In dynamic TG experiments at low heating rates, the hemihydrate and dihydrate contents can be estimated from separate mass change steps of the respective dehydration reactions shown in the resulting TG curves.

Fig. 1 shows a typical dynamic TG curve of plaster A, which is very similar to the dynamic TG curve of
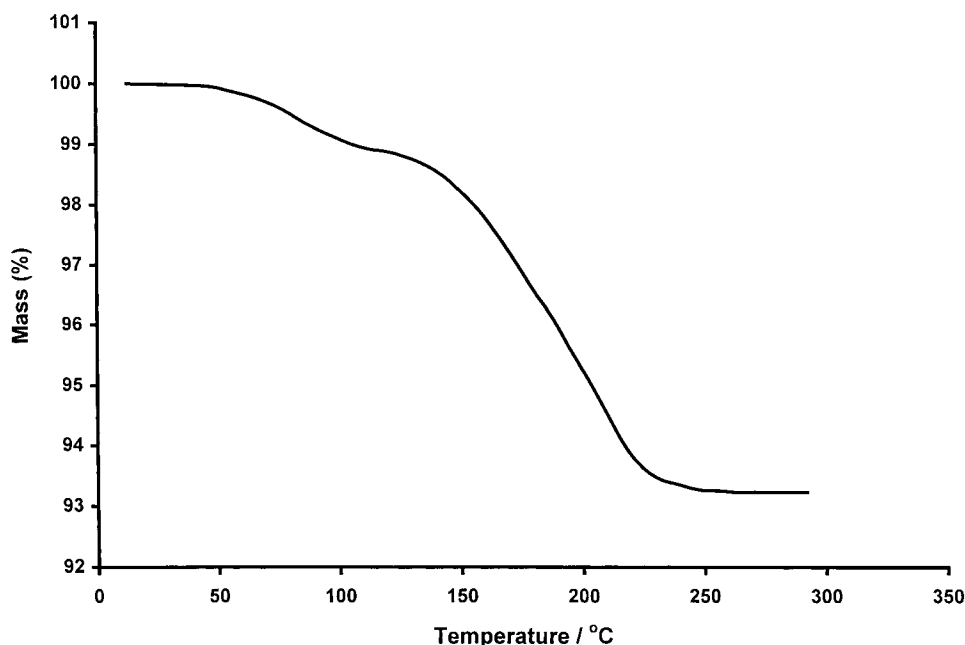
Fig. 1. Typical dynamic TG curve of 2.503 g of plaster A in air. Heating rate=5°C min⁻¹.

plaster B. It is possible to observe two steps of mass loss, the first related to reaction R-1, due to the partial dehydration of some calcium sulfate dihydrate, and the second, to the dehydration of calcium sulfate hemihydrate according to the reaction R-2. It is important to note that the second step is due to the hemihydrate present in the original sample, and also to that formed during the first step of decomposition. The end of the first step must be estimated, because of the overlap with the beginning of the second step.

$$CaSO_4 \cdot 1/2H_2O \rightleftharpoons CaSO_4$$
$$= 1/2H_2O \, (\text{mass loss} = 0.20\%) \quad \text{(R-2)}$$
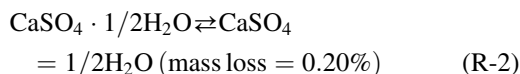
Defining DMI and DM2 as the mass % losses of the original sample in steps 1 and 2, respectively, estimated by the TG curves: H as the mass % of the hemihydrated calcium sulfate in the sample; D, the mass % of the dihydrated calcium sulfate in the sample: and I, the mass % content of the inerts in the sample; the values of H, D and I can be calculated by Eqs. (1), (2) and (3)

$$D = \text{DM1}/0.1571 \quad (1)$$
$$H = (\text{DM2} - 0.062.D)/0.062 \quad (2)$$

$$I = 100 - (D + H) \quad (3)$$

4. Isothermal TG method

During isothermal runs the dihydrate and hemihydrate salts are decomposed simultaneously according to reactions R-1 and R-2, due to the temperatures of the experiments (250°C, 275°C and 300°C). Therefore, the isothermal TG curves show the cumulative overlapping mass losses for those reactions. It is thus necessary to run two different analyses which are discussed in the following sections.

4.1. Analysis of the original sample

Fig. 2 shows a typical isothermal TG curve for an original sample A at 250°C. When the furnace reaches the desired temperature, which is shown in real time on the screen of the monitor of the prototype, the crucible containing the sample, is taken from the balance plate, where it was at ambient temperature, and is introduced into the heating chamber through the furnace door. The top curve of Fig. 2 shows the change
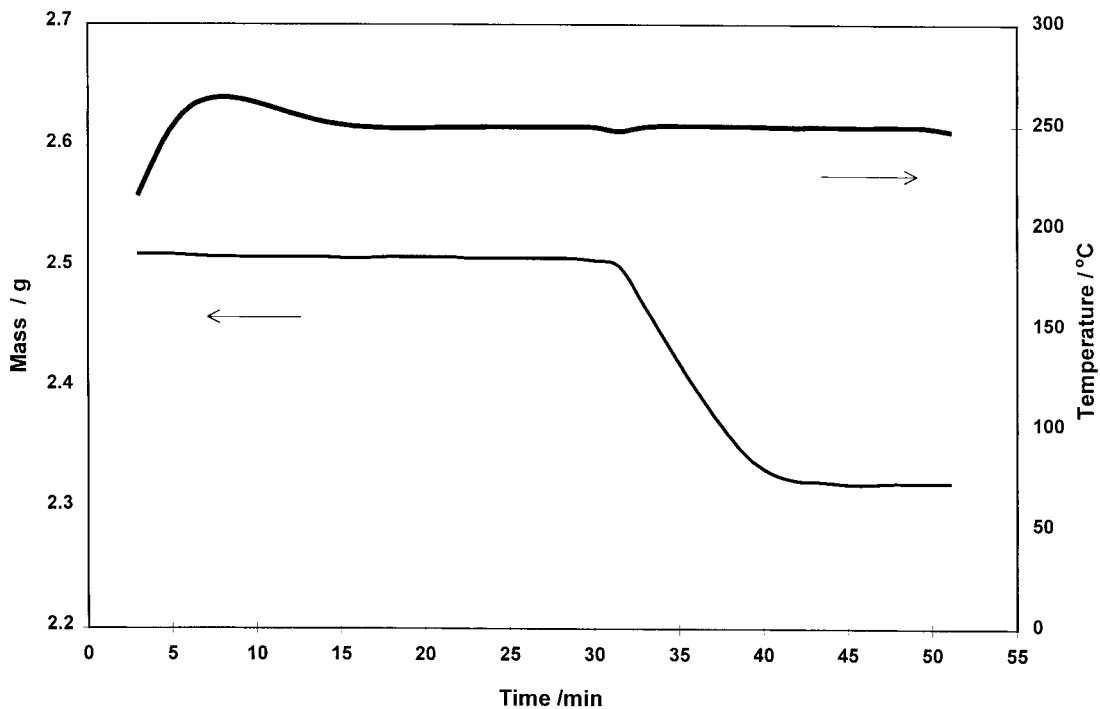
Fig. 2. Typical isothermal TG curve of plaster A at 250°C.

of temperature in the heating chamber of the furnace, and the lower curve shows the sample mass, both plotted vs. time.

If DM is the total mass % loss during the isothermal analysis of the original sample, it can be seen, by the system of Eqs. (4) and (5), that the calculation of D, H and I depends on the complementary data which will be given by the analysis discussed in Section 4.2

$$0.062 \cdot H + 0.2091 \cdot D = DM \tag{4}$$

$$I = 100 - H - D \tag{5}$$

4.2. Analysis of the modified sample

For the second analysis a modified sample is prepared. The original sample is first hydrated with water equivalent to 70% of its mass, to have the usual consistency of plaster molds as recommended by the manufacturers. After drying the hydrated sample at 45°C to constant mass [3], isothermal experiments were carried with about 2.5 g taken from this modified sample. Isothermal TG curves of the hydrated and dried samples are similar in shape to that shown in Fig. 2. Total dehydration (reaction R-3) of the calcium sulfate dihydrate occurs.

$$CaSO_4 \cdot 2H_2O \rightleftarrows CaSO_4$$
$$+ 2H_2O \, (\text{mass loss} = 20.91\%) \tag{R-3}$$
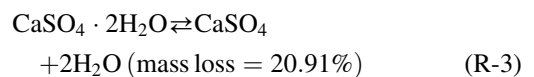
The apparent inert content I^* can be estimated by the Eq. (6), where DMC is the total measured mass % loss. The expression in parentheses represents the mass % content of the total calcium sulfate dihydrate in the modified plaster sample.

$$I^* = 100 - (100 \cdot DMC / 20.91) \tag{6}$$

Due to the total hydration which occurs initially in this treatment, the original masses of the hydrated and dried samples are increased by the amount of reacted water. Therefore, the actual inert content in the original sample is given by

$$I = I^* \cdot (1 + 0.001862 \cdot H) \tag{7}$$

Table 1
Measured and calculated parameters of dynamic thermogravimetry of original plaster samples

Sample	First mass loss DMI (%)	Second mass loss DM2 (%)	$CaSO_4·1/2H_2O$ content (%)	$CaSO_4·2H_2O$ content (%)	Inert content (%)
A1	0.92	5.88	88.98	5.86	5.16
A2	0.95	5.86	88.47	6.05	5.48
A3	0.93	5.83	88.11	5.92	5.97
B1	1.10	5.76	85.90	7.00	7.10
B2	1.20	5.72	84.62	7.64	7.74
B3	1.14	5.74	85.32	7.26	7.42

Solving the system of equations Eqs. (4), (5), (6) and (7), the calcium sulfate hemihydrate content of the original sample is given by Eq. (8). Then D and I are calculated, respectively, by Eqs. (4) and (5).

$$H = (DMC - DM)/(0.18603 - 0.001862 \cdot DMC) \quad (8)$$

5. Results and discussion

Dynamic TG results are given in Table 1. As can be seen, the mean value obtained for the hemihydrated calcium sulfate content of plaster A is 88.51%, whereas for plaster B it is 85.28%. The respective mean contents of dihydrated calcium sulfate are 5.94% and 7.30%. It is interesting to note that in other characterization analyses made with the same original samples [13], the time of setting for plaster B was higher than that of plaster A. That could be explained by the higher mean inert content found in plaster B which was 7.42 mass %, when compared to the 5.54 mass % of inerts of plaster A, assuming that one of its components is a setting retardant.

Table 2 shows the measured and calculated data relative to isothermal analyses of the respective original samples taken directly from the plastic bags. Table 3 shows the data relative to the isothermal analyses of the modified samples of plaster types A and B. The mean inert content values of both plasters, calculated by this method, are similar to those calculated in the former method, but a difference is observed for the contents of the hydrated salts which shows a higher dihydrated calcium sulfate content. This difference is probably due to the fact that in dynamic analyses the respective mass losses due to the dehydrations (DM1 and DM2) must be estimated, and in the isothermal runs, the total measured mass losses of the original and modified samples (DM and DMC) do not depend on any such estimations.

6. Conclusions

Thermogravimetry can be used for quality control of commercial plasters either by dynamic or isothermal methods, and the partial hydration of the plasters which have not been well stored, can be detected.

Table 2
Measured and calculated parameters of isothermal TG of original plaster samples

Sample	Temperature/°C	Total mass loss DM (%)	$CaSO_4·1/2H_2O$ content (%)	$CaSO_4·2H_2O$ content (%)	Inert content (%)
A1	250	7.27	84.96	9.58	5.47
A2	275	7.29	85.26	9.58	5.16
A3	300	7.29	85.57	9.49	4.94
B1	250	7.15	83.38	9.47	7.15
B2	275	7.20	82.29	10.03	7.68
B3	300	7.22	81.94	10.23	7.83

Table 3
Measured and calculated parameters of isothermal TG of plaster samples after hydration and drying steps

Sample	Temperature/°C	Total mass loss DMC (%)	Apparent inert content (%)
A1	250	19.92	4.72
A2	275	19.98	4.45
A3	300	20.02	4.26
B1	250	19.62	6.19
B2	275	19.52	6.66
B3	300	19.49	6.79

Dynamic TG allows a direct estimation of the dihydrated calcium sulfate, hemihydrated calcium sulfate and inert contents of commercial plasters.

Isothermal TG measures those contents combining the analysis of the original sample with that of a modified one, obtained after hydrating and drying steps of the original plaster.

The isothermal method is recommended rather than the dynamic one, because it allows measurements which do not depend on any estimation of mass loss, and can also be used as a conventional laboratory procedure for the quality control of commercial plasters.

Acknowledgements

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