TA Instruments

Thermal Analysis & Rheology

THERMAL SOLUTIONS

TGA Characterization of Gypsum in Stucco

PROBLEM

Stucco (calcium sulfate hemihydrate) has great commercial significance as a construction material for buildings, etc. Stucco is formed by partial dehydration of gypsum (calcium sulfate dihydrate), a naturally occurring mineral. It is important to control this dehydration process since the presence of small amounts of residual gypsum (<1%) in the final stucco can adversely affect its strength in end-use. However, neither chemical nor x-ray diffraction techniques are able to provide quantitation of gypsum at the levels required.

SOLUTION

On the other hand, thermogravimetric analysis (TGA), which measures weight changes in materials as a function of temperature, should provide a convenient method for quantifying the amount of gypsum present based on the weight loss which occurs during the first stage of dehydration, provided the successive weight losses associated with the two different stages of dehydration (shown below) are sufficiently resolved to allow accurate, reproducible quantitation.

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2\ H_2O + 1\ 1/2\ H_2O \rightarrow CaSO_4 + H_2O$$

(gypsum) (stucco) (anhydrite)

Figure 1 shows the TGA profile for the dehydration of pure gypsum when heated at 10°C /minute. The parent weight loss curve (solid line) indicates what appears to be a single weight loss between 100 and 170°C. However, the magnitude of this weight loss (about 22% of the original sample weight) agrees well with what is stoichiometrically expected for complete dehydration of the gypsum to the anhydrite form. Examination of the weight loss derivative curve (dashed line), which usually is a more sensitive

Figure 1 - Weight Loss Profile For Calcium Sulfate Dihydrate - Open Pan

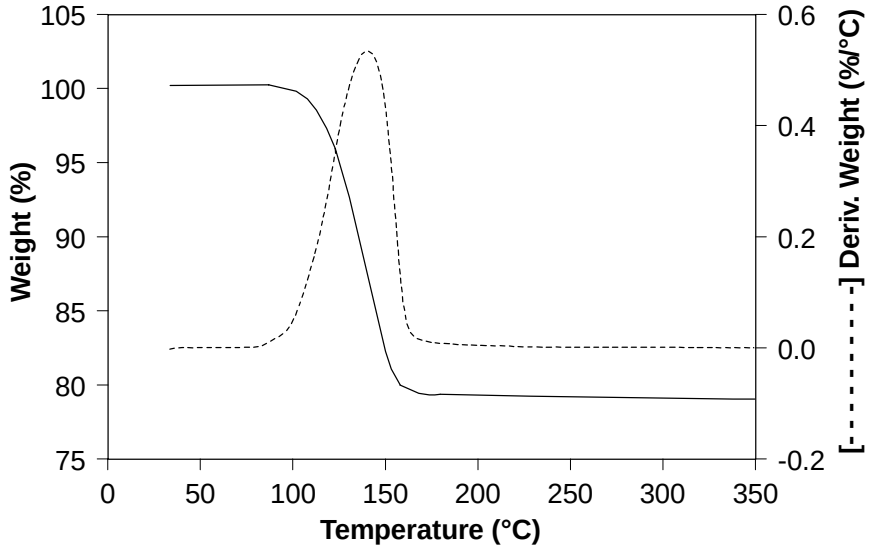
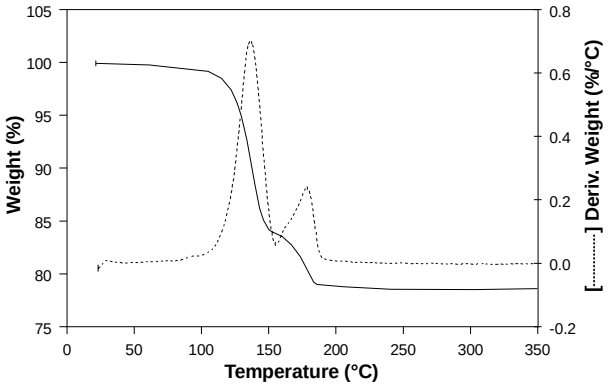


Figure 2 - Weight Loss Profile For Calcium Sulfate Dihydrate - Closed Pan with Pinhole



indicator of the presence of closely occurring multiple weight losses, also indicates apparently only one weight loss. Furthermore, even the use of slower heating rates and smaller samples does not improve resolution sufficiently to see the two weight losses.

Duval [1] has shown, however, that the resolution of successive TGA dehydration steps can be achieved by increasing the vapor pressure of water in the purge gas around the sample because the increased moisture above the sample effectively suppresses the dehydration processes and moves them to higher temperatures. Earlier studies on calcium sulfate hydrates using DSC evaluations in a sealed hermetic pan with a pinhole [2] indicate that that approach achieves similar results to the approach of Duval since the moisture evolved during the first stage of dehydration remains in the "head space" above the sample and suppresses the second stage. Therefore, it seems reasonable that use of these "modified" DSC pans* in conjunction with TGA (i.e., the sample is loaded into the DSC pan and then that pan is put into the TGA sample pan) may solve the weight loss resolution problem for calcium sulfate hydrates. Figure 2 shows that the successive weight losses are in fact resolved by this approach, yielding the expected stoichiometric results.

In the case of pure gypsum, both weight losses should, of course, be present. In properly processed stucco, on the other hand, the presence of the first dehydration weight loss is undesirable because it indicates the presence of residual gypsum. Figure 3, for example, shows the TGA profile for a stucco deliberately prepared to contain 2% gypsum evaluated using the TGA/pinhole DSC pan approach. Good resolution is observed between the two weight loss regions and a clean measurement is provided for the respective weight losses.

Figure 3 - Weight Loss Profile For 2% Gypsum in Stucco - Closed Pan with 75μm Hole

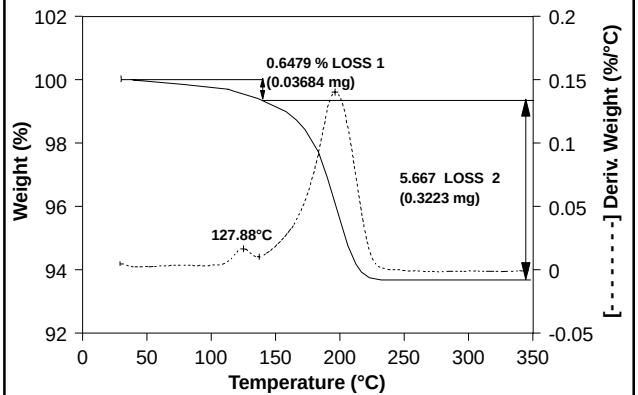


Figure 4 - Working Curve for the Determination of Gypsum in Stucco

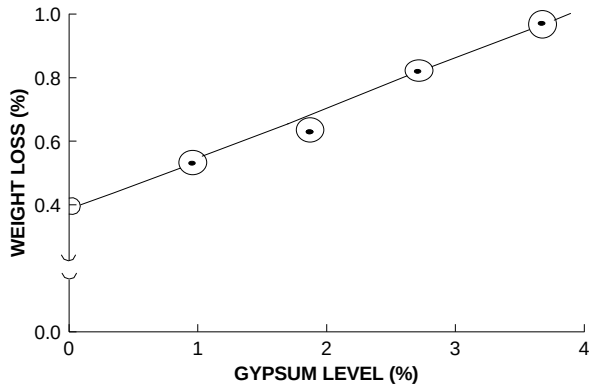
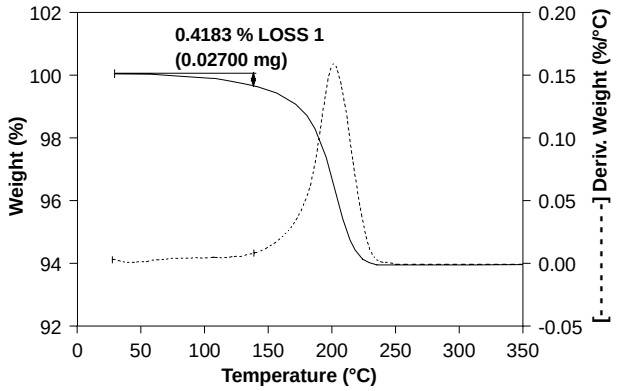


Figure 5 - Weight Loss Profile For Calcium Sulfate Hemihydrate - Closed Pan with 75μm Hole



For analytical purposes, a calibration curve must be created relating the observed initial TGA weight loss to percent gypsum in stucco. This curve is prepared by characterizing (using the pinhole pan procedure) a series of reference materials prepared to cover the anticipated range of the test method. A typical resultant curve (with a linear correlation coefficient of 0.995) is shown in Figure 4. This calibration curve has an offset and does not pass through zero. The reason for this offset is seen in the weight loss profile for pure stucco shown in Figure 5. The figure shows that pure stucco loses weight even at temperatures as low as 50°C. Thus, the two TGA weight losses overlap leading to the non-zero intercept of the calibration curve.

Using this calibration curve, levels as low as 0.5% dehydrate may be determined in the hemihydrate. A high sensitivity and precise TGA (such as the TA Instruments TGA 2950 or TGA 2050) is required to perform such a measurement since a stucco containing 0.5% gypsum impurity produces only a 0.08% initial weight loss.

* DSC hermetic pan lids with 75μm pinhole (TA Instruments P/N 900860-901).

REFERENCES

1. C. Duval, J. Lecomte, C. Pain, Compt Rend, 245, 1514 (1957)
2. TA Instruments Publication Number TS-26

ACKNOWLEDGMENT

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