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TG-DTA DETERMINATION OF WATER EVOLVED FROM $CaSO_4{\cdot}xH_2O$

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Abstract

To improve the separation of the dihydrate and hemihydrate phases, different sample masses, heating rates and crucibles were used. A TG-DTA method was developed for the determination of water evolved from $CaSO_4{\cdot}xH_2O$. The new crucible introduced for the Q-1500D MOM derivatograph gives a possibility for the evolved water to be determined independently from the TG and DTA curves.

Keywords: calcium sulphate, dehydration, thermogravimetry

Introduction

The TG-DTA quantitative determination of differently coordinated crystallization water encounters certain experimental obstacles [1–10]. This is a result of the frequent partial overlapping and difficulty of distinction of the separate stages and thermal effects [1–20]. Optimization of the experimental conditions can be achieved by using various types of TG-DTA techniques. With the MOM derivatograph, a successful separation of the TG curves of the crystal forms is possible with the labyrinth crucible described by Paulik [6, 7]. However, with this device no information is obtained about the enthalpy processes of the system. The best results with the TG method are attained by using the labyrinth crucible.

In the present study, a new type of crucible is proposed for simultaneous phase separation from the TG curve and to obtain information on the enthalpy changes from the DTA curves. On this basis, a simultaneous TG-DTA method for determination of the crystal forms of $CaSO_4{\cdot}xH_2O$ is described.

Experimental

The MOM Q-1500D derivatograph and pure $CaSO_4{\cdot}xH_2O$ from Merck were used. In studies to establish the most favourable conditions for precise determi-

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nation of the contents of the crystal forms, the parameters were varied as follows:

- type and rate of flow of gas (argon 5, 10, 15 and 20 l/h).

Experiments were also performed under static air conditions.

- sample mass (100, 200, 300, 500 and 800 mg);
- rate of heating (2.5, 5 and 10 deg·min^{-1});
- type and geometric size of crucible (cf. Fig. 1).

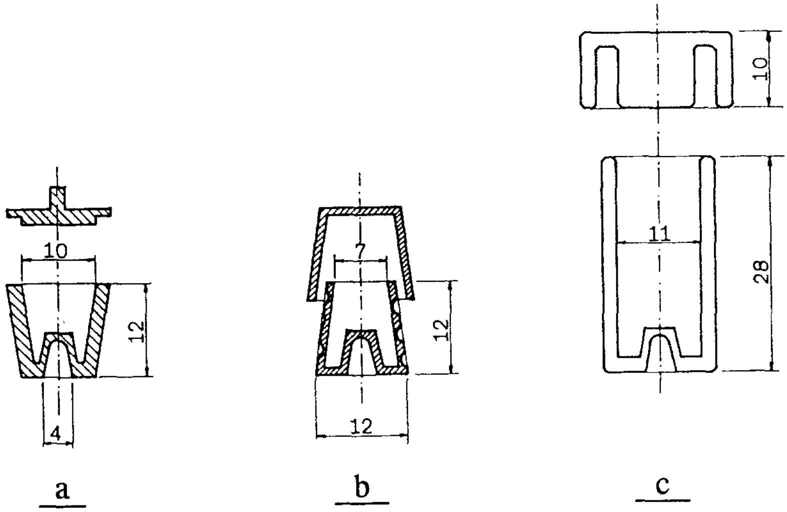

Fig. 1 Typical crucibles: a. ceramical type; b. labyrinth type; c. cylindrical type

Results and discussion

The results of the preliminary tests showed that a better phase separation is obtained without a gas flow, at a heating rate of 2.5 deg·min^{-1} and with a sample mass of 500–800 mg.

Figures 2 and 3 depict TG-DTA curves obtained by using a standard ceramic crucible with the shape of a truncated cone and the same crucible with a standard lid. It is obvious that the phase transition from the dihydrate to the hemihydrate is most obscured when a standard ceramic crucible, with or without a lid, is used. Neither the TG nor the DTA curves permit determination of the quantity of dihydrate during the intermediate transition stage when the hemihydrate product is formed. This is due to overlapping of the final period of the dehydration process (resulting in the hemihydrate product) with the starting period of the dehydration stage, when the transition from the hemihydrate to the anhydrous salt takes place. This means that this type of crucible can not be used for quantitative determination of mixtures of the dihydrate and hemihydrate.

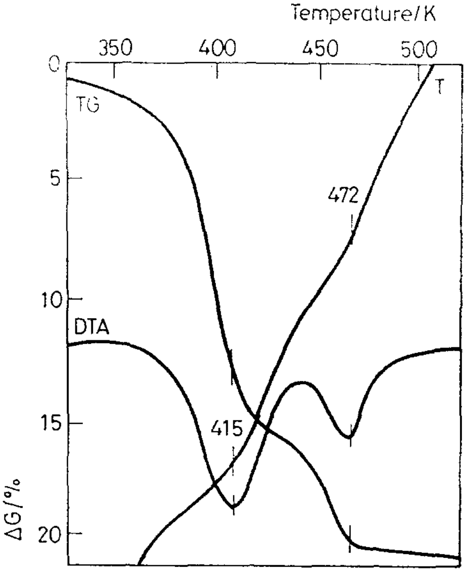

Fig. 2 TG, DTG and DTA curves of $CaSO_4 \cdot xH_2O$. Heating rate −2.5 deg·min^{-1}; W_a=500 mg; S_b=200 mg; Crucible: a

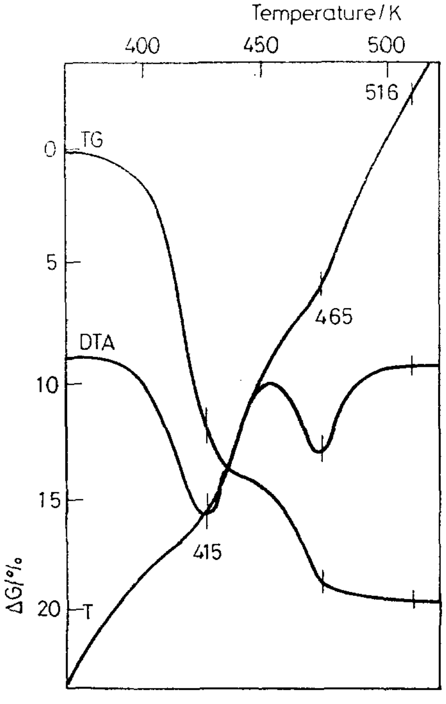

Fig. 3 TG, DTG and DTA curves of $CaSO_4 \cdot xH_2O$. heating rate −2.5 deg·min^{-1}; W_a=500 mg; S_b=200 mg; Crucible: a. with two lids

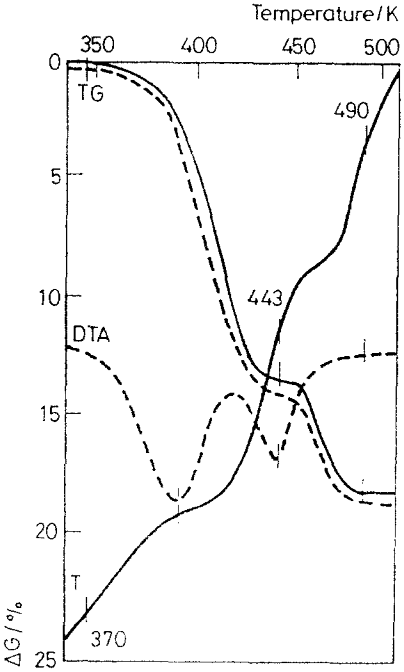

Fig. 4 TG, DTG and DTA curves of $CaSO_4 \cdot xH_2O$. Heating rate –2.5 deg·min^{-1}; W_a=500 mg; S_b=200 mg; Crucible: b

A labyrinth crucible and a quartz cylindrical crucible with a new lid were used for the experiments shown in Figs 4 and 5. Use of the labyrinth crucible (Fig. 4) yielded a TG curve reflecting a better separation of the crystallization water evolved from the hemihydrate. The relative error from a triple repetition of the experiment was under 1%, with a maximum deviation of 5% between the tests. These results are much better than those obtained with the recommended procedure [4, 5, 11].

The cylindrical quartz crucible with a new lid and a sample mass of 500 mg (Fig. 4) allows an identical separation of the water evolved. This is analogous to the case with the labyrinth crucible involving the simultaneous corresponding enthalpy change from the DTA curve. Increase of the sample mass up to 800 mg (Fig. 5) did not result in a corresponding increase in the measurement precision. Higher temperature deviations were recorded, but these were a natural consequence of the heat increase during the dehydration process. The results are well reproducible, with a maximum deviation of 5% between the test results from the TG and DTA curves.

Conclusions

The presented studies clearly demonstrate that the proposed quartz cylindrical crucible with a lid can be successfully used for the quantitative determina-

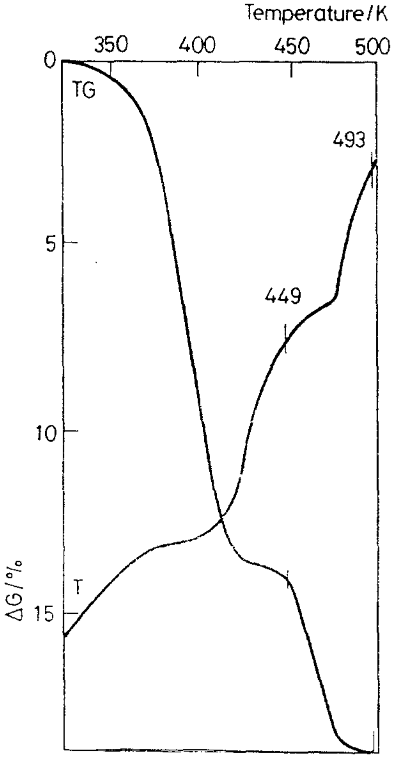

Fig. 5 TG, DTG and DTA curves of $CaSO_4{\cdot}xH_2O$. Heating rate –2.5 deg·min^{-1}; W_s=800 mg; S_b=200 mg; Crucible: c

tion of crystallization water in calcium sulphate. The best conditions for studying the dehydration of $CaSO_4{\cdot}xH_2O$ involve the use of a cylindrical crucible at a heating rate of 2.5 deg·min^{-1} and a sensitivity of 200 mg under static air conditions. The results are well reproducible, with a maximal deviation of 5% between the test results from the TG and DTA curves. Increase of the sample mass up to 800 mg does not result in a corresponding increase in measurement precision. This crucible can be applied widely to study the dehydration of other crystal hydrates where the partial pressure of water vapour plays a determinant role as concerns the kinetics of the process.

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