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THE STUDY OF HYDROTHERMAL PROCESSES BY THE DIFFERENTIAL THERMAL ANALYSIS METHOD

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ABSTRACT

A DTA apparatus has been developed which can operate up to pressures of 500 atm and temperatures of 500°C. A coated thermocouple (thermocoax) is used for the measurement of temperature differences. Thermograms for the dehydration of gypsum, hydration of cement paste and hydrothermal synthesis of calcium silicates hydrates are shown to demonstrate the capability of the apparatus.

INTRODUCTION

The reaction of water with solids plays an important role in many industrial processes. Examples are: the dehydration of gypsum to hemihydrate in the medium of liquid water, which is the basis of the production of plaster of Paris[1]; the hardening of cement pastes[2] at normal temperature or in an autoclave; the synthesis of molecular sieves[3], etc.

A temperature above 100 °C is needed for some of these processes and the closed bomb must be used. All methods studying such processes are very difficult[3].

DTA represents a relatively simple experimental technique which has been little used in this field[4–7] until recently, in spite of its great advantage in that it enables to record reversible processes in the studied system. An apparatus for DTA in which the pressure is generated internally has been developed.

DESCRIPTION OF APPARATUS

The pressure vessel (A) (see Fig. 1) is a cylinder made of austenitic stainless steel (Poldi AKVS). The stopper B is cone shaped and its angle is smaller (difference of 1°) than that of the conical hole in the cylinder (A). The contact area of the stopper (B) and the autoclave (A) is so small that the elastic deformation is sufficient to provide perfect tightness. By means of a screw C, which is fitted with a planparallel ring (D), the closure (B) is pushed against the conical autoclave jacket wall. When opening the autoclave, the screw (C) is revolved and the closure (B) is withdrawn by turning the screw (E). For very high pressures the Bridgman closure is more suitable[5].

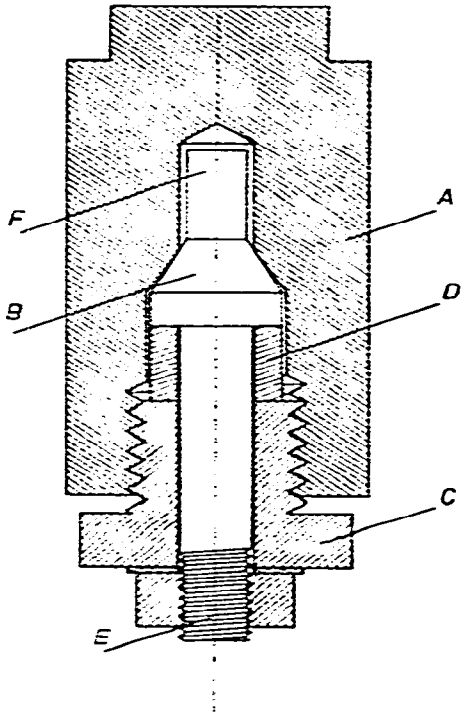

Fig. 1. Apparatus for DTA (axial section). A = Closed bomb; B = stopper; C = closing screw; D = slip ring; E = screw for autoclave opening; F = sample holder.

The measuring device is connected with the body (B), as can be seen from Fig. 2a. Tube (A) forms a cylindrical hollow at the end of the stopper (B). This hollow is divided by a plot (C) into two chambers: one for a sample and the other for the standard material. The thermocouples covered with a coat of stainless steel* are sealed into two holes in the stopper (B) and their joints are situated in two chambers for a sample and the standard, respectively (see Fig. 2b). Both thermocouples are drawn through the tube (E) in which the third thermocouple (F) for the temperature measurements is also placed (see Fig. 2b). For the study of liquid systems the special sample holders are suitable. Two types are shown in Figs. 3a and 3b.

The autoclave was placed in a vertical tubular oven. The constant temperature rise (10°C min^{-1}) was controlled by the temperature program controller (Netzsch Co., G.F.R.) and for the DTA curve recording a high quality potentiometric recorder was used. The recording of temperature differences required a direct current amplifier with minimal drift.

*Thermocouples are fabricated commercially (Thermocoax–Philips, Thermocoax–Soclern, Mantel-thermoelement–Walzwerk Hettstadt D.D.R. etc.). Both wires of the thermocouple including their junction are situated in a thin tube of stainless steel and isolated with fine MgO powder.

If liquid water and its vapor are present, the pressure must correspond to the liquid/vapor equilibrium and is determined by the temperature only. For different volumes of water in the pressure vessel the actual pressure can be found in tables[6].

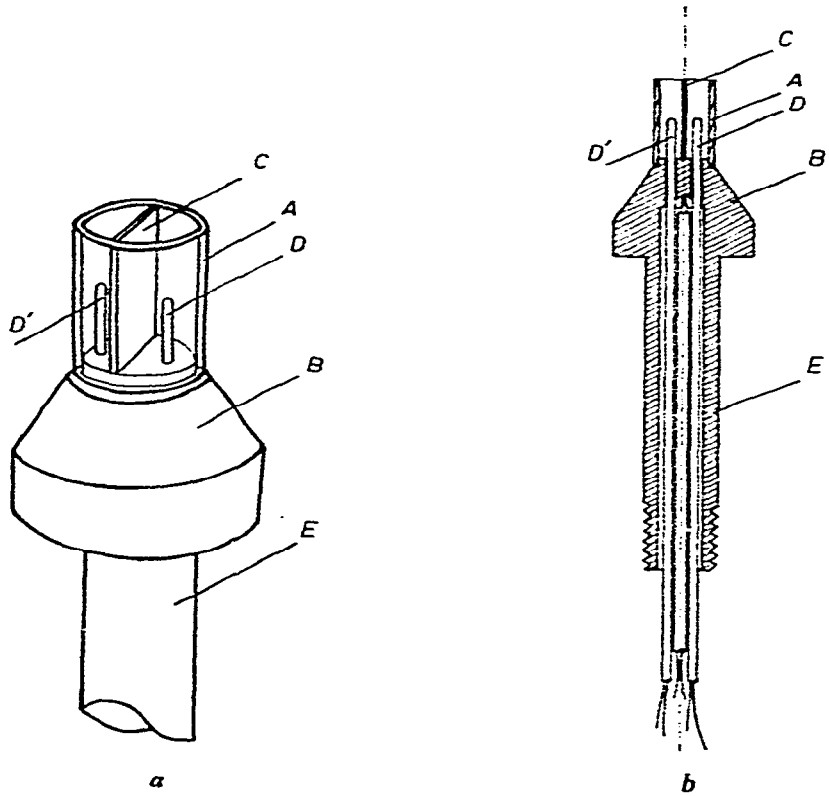

Fig. 2. (a). Measuring device. (b) Axial section of measuring device. A = Cylindrical tube—sample holder; B = stopper; C = dividing plate; DD' = thermocouples; E = neck of the stopper (for opening).

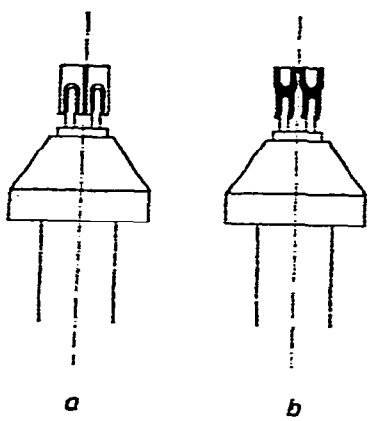

Fig. 3. Special sample holders. (a) For liquid systems. (b) For calorimetric measurements.

Once the system was set up, the operation was simple. After the standard and the sample were placed into the chambers, the autoclave was filled up to one half with water, then it was closed and placed in the oven.

RESULTS

The apparatus described for DTA is applicable to the study of equilibria and kinetics of reactions which take place under hydrothermal conditions.

As the first example the dehydration of gypsum will be shown. The DTA curve in Fig. 4 shows that the hemihydrate ($CaSO_4 \cdot 1/2H_2O$) can be prepared by dehydration of gypsum in liquid water (the first peak). At the temperature of 240 °C hemihydrate is transformed to anhydrite II (the second peak). Evidently the condition for the stability of intermediate products can be determined by the DTA method.

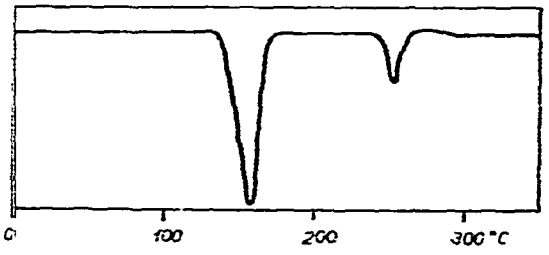

Fig. 4. DTA of gypsum in liquid water.

The process of hydration of solids such as anhydrous cement compounds is another problem which can be studied using our apparatus (Fig. 5). These processes

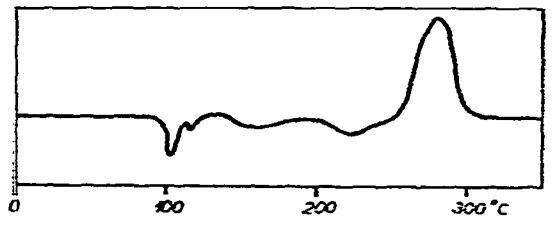

Fig. 5. DTA of portland cement paste in hydrothermal medium.

proceed very slowly at ordinary temperatures (hydration of cement paste takes about 3 years) and therefore treatment in an autoclave at 180°C is often used. Our DTA method can be recommended especially when problems occur involving the choice of different types of cements and for the optimal treatment in an autoclave.

The DTA curves of the mixture CaO–SiO_2 (in the ratio 1:1) at hydrothermal conditions (see Fig. 6) evidently show the formation of calcium silicate hydrates. The difference in behavior of SiO_2 in the form of quartz (curve 1) and fine silica gel particles (curve 2) shows the applicability of DTA for the study of such reactions.

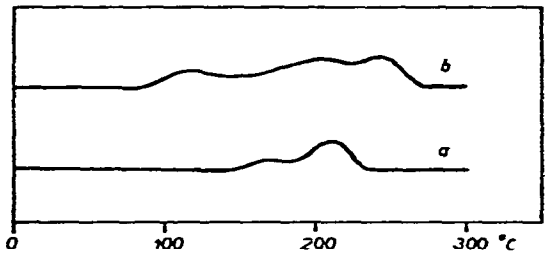

Fig. 6. DTA of the paste $Ca(OH)_2$ and SiO_2 under hydrothermal conditions. (a) SiO_2 in the form of silicagel. (b) SiO_2 in the form of fine quartz powder.

CONCLUSIONS

We have presented some results of preliminary experiments as examples of the applicability of the DTA method under high pressure. Evidently the applicability of this method is much broader, especially in the field of organic chemistry. Thermal reactions of organic solids have been regarded as a speciality of little interest to the practicing organic chemist but recently the situation in this field has changed as can be seen from a series of publications[8–10]. The DTA method can be a useful tool for research in this particular field of science.

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