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MODIFIED THERMAL ANALYSIS EQUIPMENT AND TECHNIQUE FOR STUDY UNDER CONTROLLED HUMIDITY CONDITIONS*

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ABSTRACT

An apparatus is described that enables samples to be run on both DTA and TGA with prior exposure only to a desired condition.

Results are presented for porous glass and hydrated portland cement. For porous glass the runs obtained by a vacuum sorption balance can be reproduced by thermal analysis of separately conditioned samples, and no distinction can be made between monolayer and multilayer adsorbed water. For hydrated portland cement, however, two peaks were detected and interpreted, respectively, as interlayer and adsorbed water. This supports the new model for hydrated portland cement.

INTRODUCTION

Dynamic methods of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been extensively applied in clay mineral studies and recently have attained great importance in inorganic chemistry[1-8]. As these techniques are applied in diverse fields, there is a continuous demand for special types of equipment that will suit a particular field of activity. This demand has resulted in many modified types of equipment designed to meet very special requirements.

In cement chemistry, clay mineralogy, and colloid chemistry extreme caution is required in the drying of materials prior to thermal analysis. They are very sensitive to humidity conditions. Different workers have shown variability in thermal effects, especially below 200°C, and this can be traced to different methods of drying the samples. In clay mineralogy a recent recommendation states that all clays be equilibrated to 56% RH over $Ca(NO_3)_2 \cdot 4H_2O$ prior to analysis. As this salt has a high temperature coefficient, Wink and Sears[9] have suggested the use of $Mg(NO_3)_2 \cdot 6H_2O$. No attempt has been made to ensure the transference of the material at a constant temperature and humidity to the specimen container of the thermal unit.

In examining hydrated products of cements by thermal methods the drying procedure is very critical. Insufficient drying may not effectively remove the physically held water and too severe a drying may remove the chemically held water. In

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addition, exposure to carbon dioxide in a humid atmosphere may carbonate the hydrated cement. In the thermal analysis of cement pastes no uniform method of drying has yet been attempted.

Greene[10] has suggested vacuum-drying of the sample at 1 or 2 mm Hg for 2 to 3 h. Kalousek *et al.*[11] washed the samples four times with acetone, twice with ethyl ether, and dried them at a pressure of 0.01 mm for 1 h. In recent studies Kalousek recommends passing the sample through 30-mesh, inundating it in pure acetone for 3 min, suction-filtering and finally evacuating at $4–5 \times 10^{-2}$ torr for 24 h. Rey[12] has found that washing with acetone and ether and evacuation in vacuum for 6 h is insufficient to remove all the physically held water. A more efficient treatment consisted of treatment with acetone followed by five washings with ether and drying at 0.1 mm Hg for 1 h. Copeland and Hayes[13] have reported that hydrated cement pastes should be dried in a vacuum desiccator connected to a trap with dry ice at −78.5°C at a vapour pressure of 5×10^{-4} mm Hg (known as the *d*-drying method).

In general, in thermal investigations of cementitious materials the material is placed in the specimen holder at the ambient humidity and temperature conditions following an arbitrary drying procedure. Under these conditions the information obtained is of limited use.

A new model for hydrated portland cement has recently been proposed[14,15]. It is based on the fact that a large proportion of the water formerly considered to be adsorbed water is in fact interlayer water. There is thus great interest in experiments that provide a means of distinguishing between types of water, adsorbed and other, at the low temperature region of thermal analysis techniques. A technique by which samples conditioned to various humidities could be placed in equipment and maintained at a particular humidity free of interference from ambient humidity conditions and carbon dioxide would therefore be useful. By such humidity-controlled thermal analysis results could be used to plot a relation of the amount of water adsorbed at different humidities (isotherm).

This paper describes a method of carrying out DTA and TGA under controlled conditions of humidity. The usefulness of these techniques is illustrated by investigation of porous glass and hydrated portland cement exposed to different humidities.

EXPERIMENTAL

Equipment

DTA. — The 900-DuPont Thermal Analyzer is used for differential thermal measurements. This unit has a remote plug-in module called the calorimetric cell. Two silver cups are located in separate air cavities in a heating block in the cell. Chromel–alumel thermocouples contact the bottom of the holders. Samples are placed in disposable cups made of aluminum. A bell jar covers the cell during operation.

The cell is placed in a gloved box controlled at the required humidity and connected to the recorder through a length of shielded wire. Samples of required quantity are weighed in a balance placed in the gloved box (Fig. 1). The samples contained in disposable liners made of aluminum are then placed in the silver cup. An inert material, α-Al_2O_3, is placed in the other silver cup. The cell is covered with a bell jar and thermal curves are obtained at a heating rate of 10°C min.

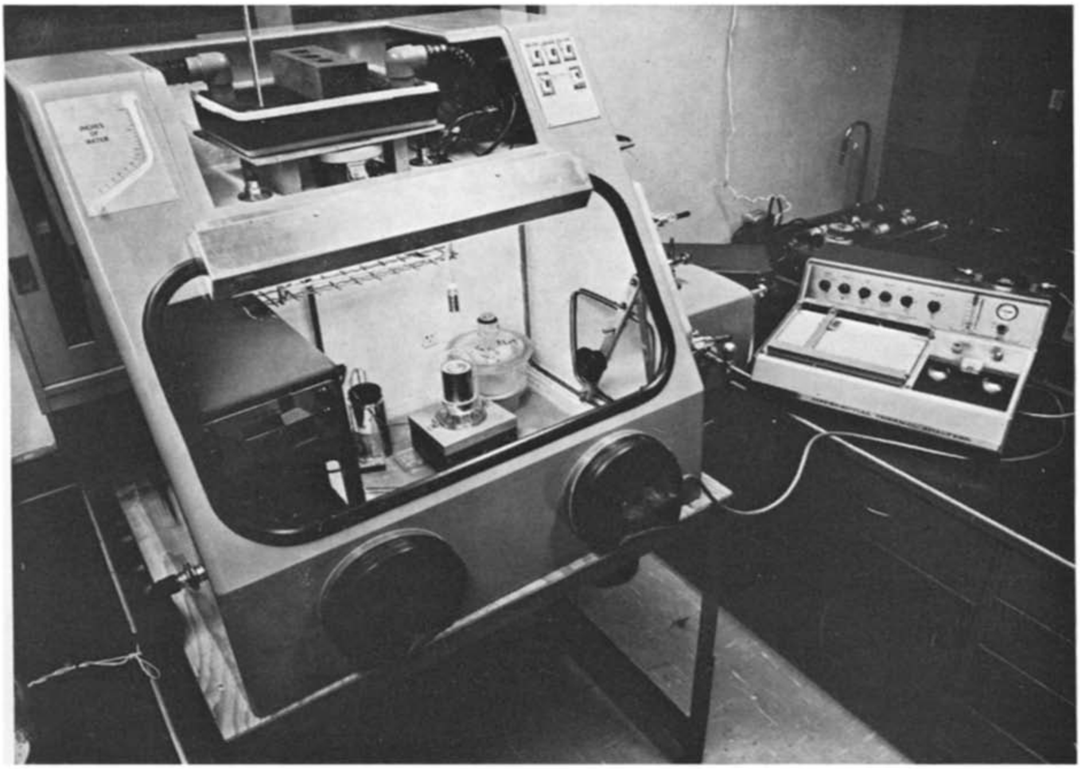

Fig. 1. DTA in a controlled humidity box.

TGA. — A gloved environmental box was constructed so that the conditioned sample could be placed in a Cahn RH electrobalance. Fig. 2 shows a schematic diagram of the box, which is constructed of lucite and is 32 × 12 × 12 in. A tube (A) on the top of the box connects the box to the balance through the position of the hang-down tube. This polyethylene tube is constructed of 4-mil film material and is fastened to the gloved box and the balance container by an O-ring and a spring clip, respectively. The hang-down tube (B) is supported by another polyfilm sac (C) at the bottom of the gloved box. A container and stirrer (D) for humidity control and a mould for making small pellets of the sample are included. The conditioning desiccator (E) containing the sample is placed in the box. When box and balance are at the required relative humidity, the desiccator is opened, the material placed in the mould and the pellet made.

The pellet is formed at low pressures to avoid loss of sample when rapid decomposition occurs. It is placed in the sample crucible (F) and a thermocouple (G) is fixed close to it. After balancing adjustments have been made, the hang-down

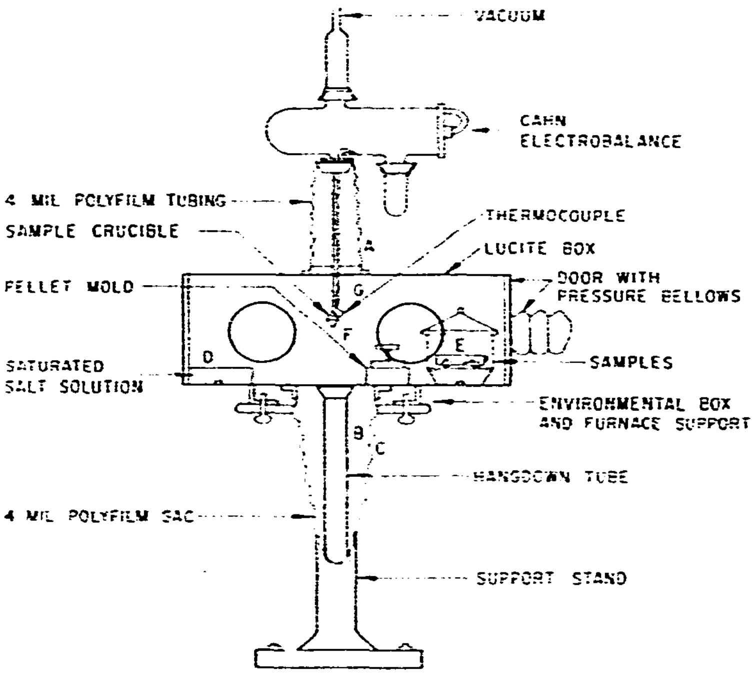

Fig. 2. Environmental glove box for mounting samples in electrobalance at controlled conditions

tube is carefully drawn up from C into A and fastened onto the Cahn balance, so that the sample is enclosed in the balance without being exposed to outside conditions. The box and connections are removed from the balance, the furnace is mounted, and the run started, usually under vacuum conditions. Figs. 3 and 4 describe the set-up with the box in position and the placement of the sample, respectively.

Materials

Porous glass (No. 7930) was supplied by Corning Glass Works in the form of 2.5-cm diameter tubes of 0.2-cm thickness. Surface area, measured by nitrogen adsorption, was 178 m^2/g. Pieces of the tube were taken for water adsorption in the high vacuum apparatus. Samples ground to pass a 100-mesh sieve and heated to 150°C for 24 h were conditioned at different humidities for DTA and TGA analysis.

Portland cement, ASTM Type II, was bottle-hydrated for 18 months at a water–solid ratio of 5. The liquid was filtered off and the cement was placed in a desiccator at 11% RH and retained for 6 months under vacuum to ensure equilibrium at this condition.

Procedure

Samples of both porous glass and hydrated cement were stored in desiccators at 11, 32, 44, 58, 65, 68, 75, 83 and 100% relative humidity obtained by using saturated solutions of various salts (Table I). Great care was taken to ensure that these humidities were attained. Stirring was essential, but could be only intermittent because heating of the solution by the magnetic stirrer caused the humidity to increase.

Samples of porous glass were taken from the 100% RH condition and placed in each of the lower conditions to obtain the desorption isotherm.

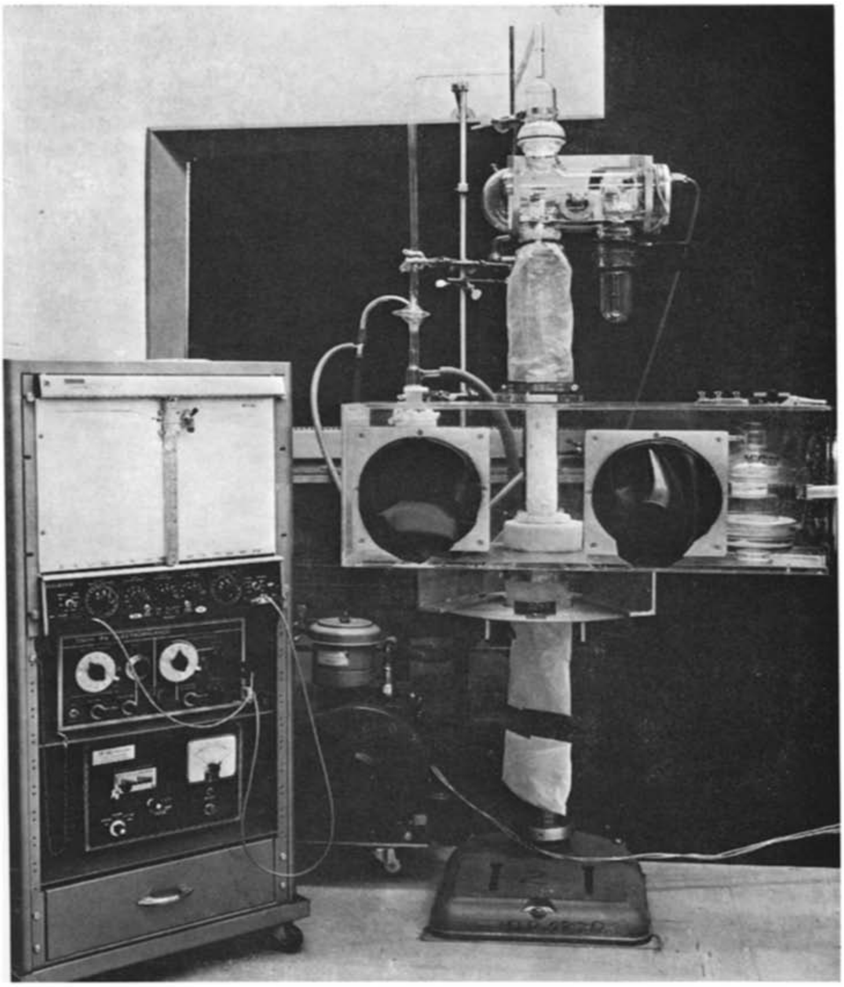

Fig. 3. TGA set-up with controlled humidity box in position.

TABLE I

SALTS USED FOR HUMIDITY CONDITIONS LISTED

Relative humidity, %	*Salt*
11	$LiCl \cdot H_2O$
32	$CaCl_2 \cdot 6H_2O$
44	$K_2CO_3 \cdot 2H_2O$
58	$NaBr \cdot 2H_2O$
65	$NaNO_2$
68	$CuCl_2 \cdot 2H_2O$
75	$NaCl$
83	KBr
100	H_2O

Fig. 4. Sample placement in electrobalance at controlled humidity.

RESULTS

DTA

Porous Glass. — Fig. 5 gives DTA curves for the samples of porous glass conditioned at humidities of 11, 32, 44, 58, 68, 75, 83 and 100% RH on both adsorption and desorption. The peak at 95 C for 11% RH grows as the humidity is increased, shifting to about 105°C, but there is no major change in the characteristics of the adsorbed monolayer (which is complete at approximately 11% RH) and the subsequently adsorbed multilayers. Fig. 6 shows a plot of peak height *vs.* relative humidity and a qualitative picture of the isotherm, including the hysteresis loop (see isotherm obtained by vacuum sorption balance, Fig. 7). Continued heating above 175°C results in a further loss of water, which is in the form of hydroxyl groups on the surface of the glass[16]. This does not result in any prominent peak and does not appear to be affected by the humidity condition.

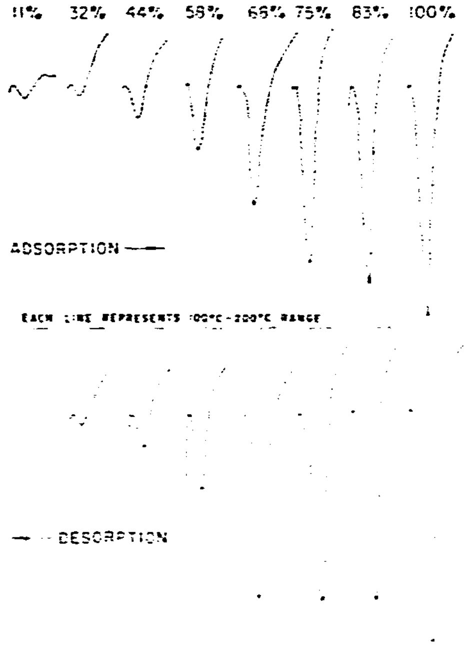

Fig. 5. DTA of porous glass conditioned at different humidities on adsorption and desorption.

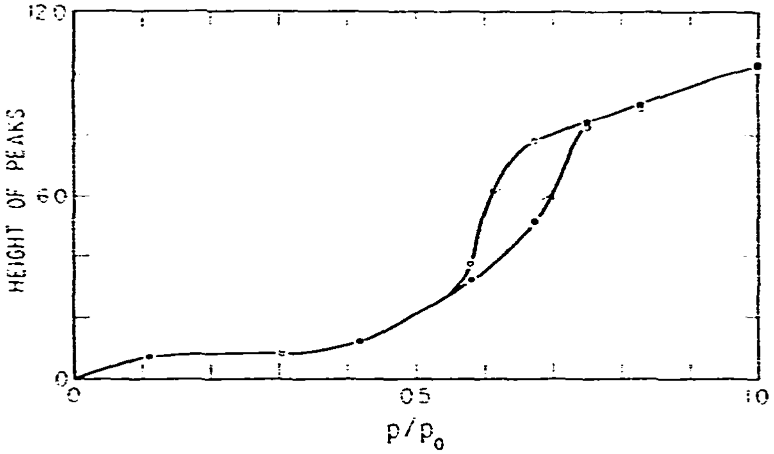

Fig. 6. Adsorption-desorption isotherms of porous glass determined by DTA.

Hydrated portland cement. — DTA curves are presented on Fig. 8, which shows the effects up to 200°C, the area of interest. Two endothermic peaks are present in all curves at different humidities; one at temperatures varying from 90 to 110°C, and growing with humidity; the other at temperatures from 120 to 150°C, and remaining relatively constant. At 11 and 32% RH the low temperature peak is present as a small shoulder, but by 43% RH it is well developed. Between 65 and 75% RH the low temperature peak has exceeded the higher temperature peak in height. Previous work[17] was not able to show this clear separation of peaks. It is considered in the present work to represent a separation of adsorbed and interlayer water. This point will be referred to again in the discussion.

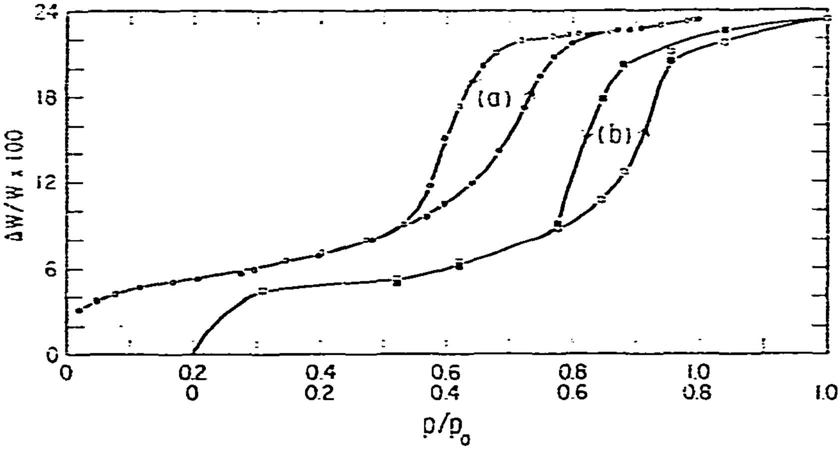

Fig. 7. Isotherms of porous glass. (a), vacuum sorption; (b), thermogravimetric analysis.

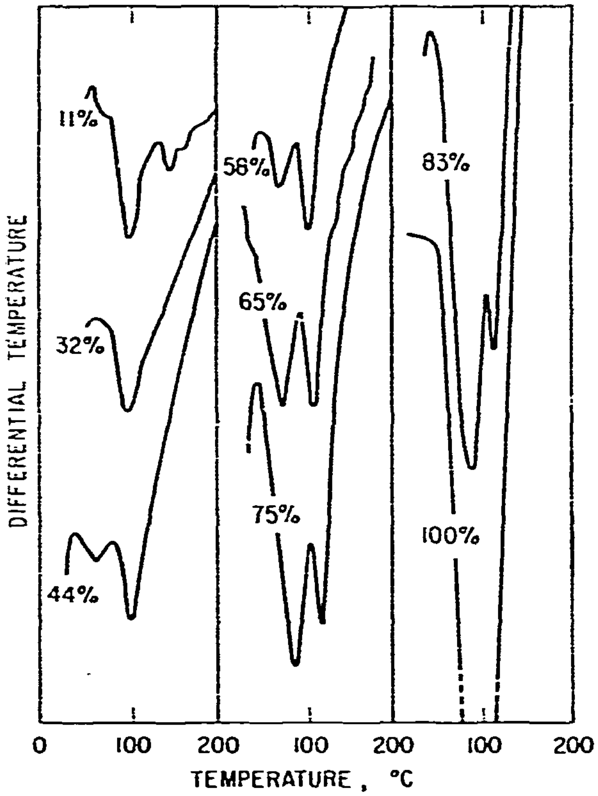

Fig. 8. DTA of portland cement paste equilibrated to different humidities.

TGA and isotherm results

Porous glass. — Two isotherms are plotted on Fig. 7. These results were obtained by vacuum sorption balance and by Cahn thermal electrobalance, respectively.

In the latter case samples were loaded into the balance at their respective humidities by means of the gloved box. It may be seen that the two methods give similar results: the hysteresis range, the total adsorbed water, and the general shape of the curve are similar. The isotherm obtained by the salt solution technique cannot be considered as reproducible as the sorption balance technique, but it is presented to show that the method of loading samples into the thermal balance works well to preserve the state and condition of the sample and thus can be used for studying the state of the water or the characteristics of unstable hydrates in the low temperature range of TGA. In the vacuum sorption balance the sample was heated at 150°C for 24 h in high vacuum before the start of the isotherm determination.

The results for TGA are shown on Fig. 9 for all samples conditioned from 11 to 100% RH. As humidity increases the weight loss in the low temperature region increases, as was observed in DTA. This rapid weight loss ends quite abruptly at approximately 180°C and is followed by a linear region of relatively low weight loss up to 650°C, where the runs were terminated. This weight loss is considered to be due to the decomposition of hydroxyl groups on the surface of the glass and not part of the physically adsorbed water. It may be observed that beyond 180°C the curves for the samples at all the relative humidity conditions are parallel, showing that relative humidity does not affect this part of the curve, *i.e.*, the quantity of chemically held water does not increase with relative humidity under these conditions. Consequently, the amount of physically held water was estimated for the thermogravimetric isotherm by the weight loss after heating to 250°C.

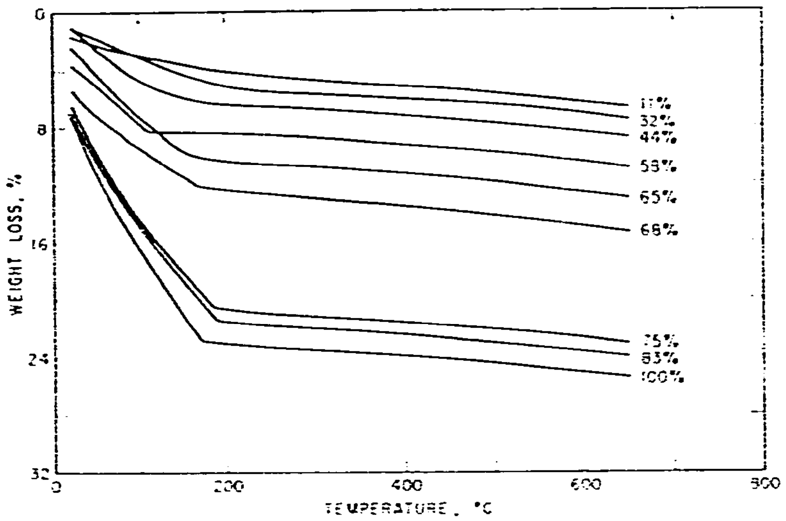

Fig. 9. Thermogravimetric analysis of porous glass conditioned at different relative humidities.

Hydrated portland cement. — TGA was performed on the same samples reported for DTA. Similar results were obtained. It was not possible to take an arbitrary temperature on the normal TGA curve and obtain weight loss giving a satisfactory isotherm. This was achieved by placing the sample in the thermal balance and heating it in vacuum at a constant temperature of 100 °C for 3 h. By this technique an isotherm was obtained very similar to that obtained by normal vacuum sorption balance techniques.

DISCUSSION

These results are only the initial stage of a wider program that includes different degrees of initial drying of samples, including *d*-drying[13] and lengthy times of conditioning. It has been shown that the technique is suitable for studying the hydrated portland cement–water system. It has also been shown that no clear difference can be observed in the DTA curves between the monolayer and multilayers of adsorbed water on porous glass. In hydrated portland cement, on the other hand, two low temperature peaks were observed, the lower of these growing from 11% RH, the higher remaining relatively constant. From previous work involving sorption and length change scanning isotherms of water on hydrated portland cement it was concluded that at 11% RH less than 10% of the total water (referred to in cement chemistry as evaporable[18]) was physically adsorbed, the remainder being mainly interlayer. This would explain the smaller low temperature peak in the DTA results. In this work also, the adsorbed water and interlayer water were equal in quantity at about 65 to 70% RH. This can be inferred by examining the DTA curves in Fig. 8, if one concludes that the low temperature peak is adsorbed water and the higher peak interlayer water.

Previous workers[17] did not obtain such a clear separation of peaks, and it must be concluded that this is due to the lack of humidity control in their thermal analysis and possibly to low sensitivity.

These results have led to further work where the samples have been dried to different degrees before conditioning. Early indications are that the results will confirm the present tentative conclusions.

CONCLUSIONS

(*1*) An apparatus has been designed that enables thermal analysis under controlled humidity conditions (both DTA and TGA) of materials that change in state or composition with humidity or react with components of the air.

(*2*) TGA and DTA analyses of porous glass reproduce an isotherm similar to that of the normal adsorption technique.

(*3*) The difference between the monolayer and multilayers of adsorbed water cannot be detected by DTA.

(*4*) Thermal analysis of hydrated portland cement produces two endothermal peaks at low temperatures, and the results allow the tentative conclusion that the lower temperature one is due to adsorbed water, the other due to interlayer water.

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