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**DIFFERENTIATION OF INTERLAYER AND
ADSORBED WATER IN HYDRATED
PORTLAND CEMENT BY THERMAL ANALYSIS**

by
R. F. Feldman and V. S. Ramachandran

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DIFFERENTIATION OF INTERLAYER AND ADSORBED
WATER IN HYDRATED PORTLAND CEMENT BY
THERMAL ANALYSIS

ANALYZED

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(Communicated by G. L. Kalousek)

ABSTRACT

Work leading to the new model of hydrated portland cement has shown that much of the water previously considered to reside on free surfaces exists as interlayer water. In the present work samples were conditioned at various relative humidities for times varying from $1\frac{1}{2}$ to 14 months and were dried to two different levels before conditioning, one being d-dry. Conditions were chosen, based on the model, so that the different states of water could be clearly illustrated. It was concluded that thermal analysis allows differentiation of interlayer and physically adsorbed water and that the different degrees of drying and very long times allowed for equilibration support all sorption results on which the new model of hydrated portland cement was based.

SOMMAIRE

Les travaux menant à la nouvelle formule de ciment portland hydraté ont démontré qu'une grande partie de l'eau qu'on croyait qui demeurerait auparavant sur les surfaces libres, existe sous forme d'entre-couche d'eau. Dans la présente étude, les échantillons ont été conditionnés à diverses humidités relatives pour des périodes de temps variant entre $1\frac{1}{2}$ mois à 14 mois, et furent soumis au séchage à deux niveaux différents avant le conditionnement, un des niveaux étant "d-dry." Les conditions furent choisies, basées sur la nouvelle formule, afin que les divers états de l'eau puissent être clairement illustrés. On en a conclu que l'analyse thermique permet la différenciation des entre-couches et de l'eau adsorbée physiquement, et que les différents degrés de séchage et les très longues périodes de temps permises pour l'équilibration supportent tous les résultats de désorption sur lesquels la nouvelle formule de ciment portland hydraté était basée.

Presented at the Second Cement Symposium held as part of the 73rd Annual Meeting of the American Ceramic Society, Chicago, April 1971.

Introduction

A new model for hydrated portland cement has been recently described (1). Portions of the model were based on results from water sorption experiments (2) and conclusions were made with regard to the state of the water and its role in the system. The model recognizes that the hydrated calcium silicates in hydrated portland cement are layer-structured but poorly oriented, and with a spacing between layers that may vary from region to region. Much of the water which had previously been considered to reside on free surfaces is now considered to exist as interlayer water, and many of the physical and mechanical properties of hydrated portland cement are ascribed to this.

The model has aroused considerable interest but doubts have been expressed (3). In a continuing research program at the National Research Council on the new model, significant new evidence was developed on the manner in which water occurs in C-S-H. In work on cements so far reported no systematic work seems to have been done on the thermal analysis of samples at controlled conditions of humidity (4, 5). However, thermal analysis of samples equilibrated at different relative humidities, based on the model, clearly differentiates between adsorbed and interlayer water. The results are presented in this report.

Experimental

Materials

A Type I portland cement was bottle-hydrated for $1\frac{1}{2}$ years at a water-to-solid ratio of 5. It was almost completely hydrated; carbon dioxide content was 1% and the surface area by nitrogen adsorption was $22 \text{ m}^2/\text{gm}$. The bottle-hydrated powder was dried to 11% R.H. and screened over a 100-mesh sieve. The residue of large Ca(OH)_2 crystals was ground and remixed with the powder.

Sample Conditioning

The bottle-hydrated powder was restored at 11% R.H. (over saturated solution of LiCl) in a desiccator for 6 months and designated prep-

aration A. One portion of A was spread 2 to 3 mm thick in dishes and placed in a large desiccator with a large-diameter tube fixed to the lid. The tube led to a pumping system which consisted of a trap cooled with solid CO_2 and a two-stage rotary pump. This corresponds to the well-known d-drying procedure. After 5 weeks of pumping the material was placed in a vacuum vessel and heated for 3 hr at 100°C . This sample is designated preparation B. Another portion of A designated preparation C was placed in a vacuum vessel and heated to 70°C for approximately 2 hr. It was found to contain approximately 3% more water than the d-dried sample. Small amounts of preparations A, B and C were placed in desiccators over saturated salt solutions (intermittently stirred by magnetic stirrers) to control at 11, 32, 44, 58, 66, 76, 84 and 100% R.H., respectively. After a period of time samples of preparations B and C exposed at different humidities as described above were placed in another vacuum desiccator conditioned at 11% R.H. These reconditioned samples were designated B(R) and C(R). The schema below illustrates how the samples were designated and their history.

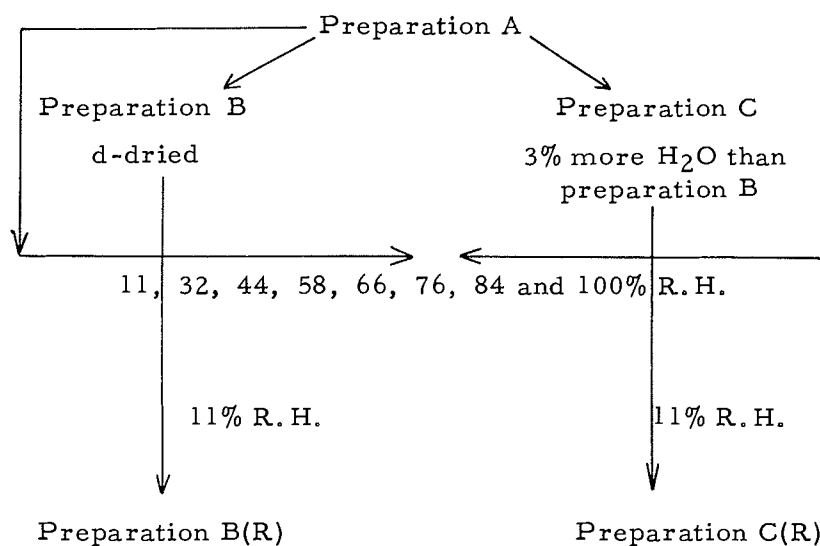


Table I shows the length of time samples of preparations A, B, C, B(R) and C(R) were held at each condition before they were analyzed. As can be seen, the times were usually about several months. Entries in the columns under TGA and DTA show when samples were tested by each technique.

WATER, INTERLAYER, ADSORBED, THERMAL ANALYSIS

TABLE I

Periods (in Months) During Which Samples Were
Conditioned at Respective Relative Humidities

Exposed at % R.H.	A		B		B(R)		C		C(R)	
	DTA	TGA	DTA	TGA	DTA	TGA	DTA	TGA	DTA	TGA
11	12-14	14-16	3-6	1.25	4.25-6.25	2.75	7-9	9-11	3	3
Back to 11% R.H.	—	—	—	—	3-5	1.50	—	—	4-6	7
32	7-9	—	3-6	1.25	1.25	1.25	7-9	9-11	3	3
Back to 11% R.H.	—	—	—	—	3-5	1.50	—	—	4-6	7
44	7-9	9-11	3-6	1.25	1.25	1.25	7-9	9-11	3	3
Back to 11% R.H.	—	—	—	—	3-5	1.50	—	—	4-6	7
58	7-9	9-11	3-6	1.25	1.25	1.25	7-9	9-11	3	3
Back to 11% R.H.	—	—	—	—	3-5	1.50	—	—	4-6	7
66	7-9	9-11	3-6	1.25	1.25	1.25	7-9	9-11	3	3
Back to 11% R.H.	—	—	—	—	3-5	1.50	—	—	4-6	7
76	7-9	9-11	—	—	—	—	7-9	9-11	3	3
Back to 11% R.H.	—	—	—	—	—	—	—	—	4-6	7
84	7-9	9-11	3-6	1.25	1.25	1.25	7-9	9-11	3	3
Back to 11% R.H.	—	—	—	—	3-5	1.50	—	—	4-6	7
100	7-9	9-11	3-6	1.25	1.25	1.25	7-9	9-11	3	3
Back to 11% R.H.	—	—	—	—	3-5	1.50	—	—	4-6	7

Thermal Analysis

In this work DTA and TGA were carried out under controlled conditions of humidity, the details of which have been published elsewhere (6).

(1) Thermogravimetric Analysis

A specially constructed gloved environmental box was used with a Cahn R.H. electrobalance (6). Samples could be weighed and loaded onto the balance and runs performed without the samples being exposed to outside conditions. Normal TGA runs were performed at a heating rate of 10°C/min under vacuum. Static runs were performed by heating at 100°C for 3 hr. Samples were compacted at 5000 psi to prevent blowing and loss of powder during evacuation and heating.

(2) Differential Thermal Analysis

The 900 Du Pont thermal Analyser was used for differential thermal measurements. This unit has a remote plug-in module called the calorimetric cell. 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 (16 milligrams) were weighed in a balance in

the gloved box. Thermal curves were obtained at heating rates of both 10 and 20°C/min. Results are reported here for 10°C/min only.

Results

(1) Thermogravimetric Analysis

The dynamic TGA runs did not show as clear a delineation of different types of water as the DTA curves. Hence, the TGA equipment was also used under static conditions, where the samples equilibrated at every condition were heated in vacuum for 3 hr at 100°C. It was found previously (2) that this condition was equivalent to the d-dry condition, and thus the results would yield quantitative information with regard to the amount of water in each sample above the d-dry condition. As a result the intensity of each DTA curve could be well defined for the region of "evaporable" water (7) on the basis of the above.

An advantage gained by performing the static thermal gravimetric analysis is that sorption isotherms can be constructed. These are shown in Fig. 1 for the preparations A, B and C. Another advantage is that these isotherms are constructed from samples that have been conditioned simultaneously at various humidities for $1\frac{1}{4}$ to 11 months (see Table I). This means that each point on the isotherm has been at its respective condition for that period. To accomplish this by a normal vacuum balance, the period involved would have been increased several-fold. As it turns out, these lengths of time are unnecessary in the regions investigated.

The points enabled outer boundary sorption curves to be drawn for preparations B and C, i.e. B(ads) and C(ads) respectively. From the points obtained from samples that had been exposed to various relative humidities and returned to 11% R.H. and the adsorption curve for preparation A, approximate scanning curves could be outlined. From the sample that had been returned from 100 to 11% R.H. the outer boundary desorption curve could be estimated. (This estimate is based on previous work with an identical sample (2).) The adsorption curve for preparation A was drawn on the isotherm loop of both preparations B and C. Its slope is very low, much lower than the outer boundary sorption curves for preparations B and C. As

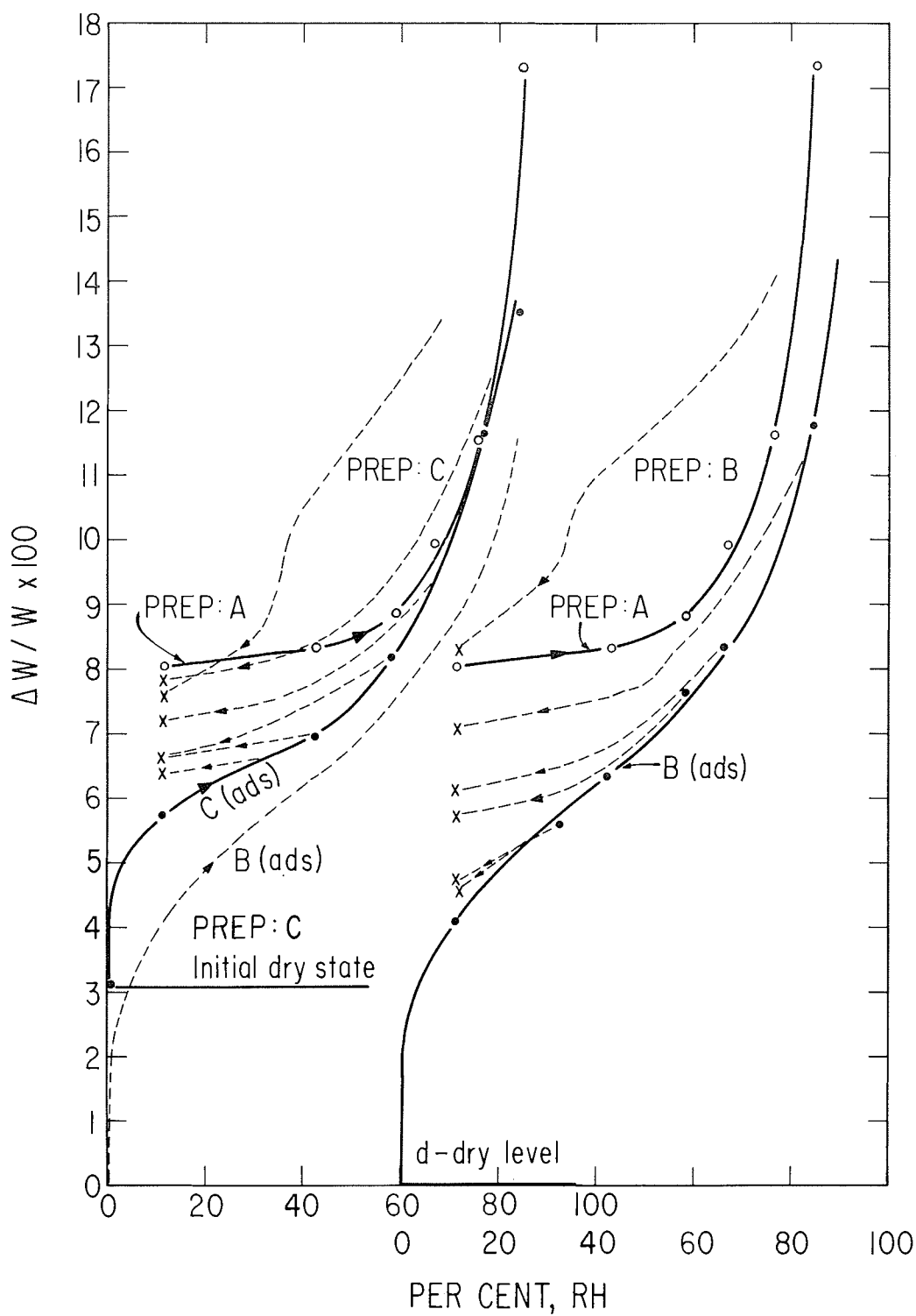


FIG. 1

Isotherms of hydrated cement from static thermal balance.

mentioned above, the scanning curves were partially located by observing the slope of this curve. Previous work (2) has already noted the difference in slope of the outer boundary curves and the scanning curves. Also shown in Fig. 1 is the fact that all the water (including hydrate water) removed when the samples are d-dried (B) or partially dried (C) from 11% R.H. is returned after the sample has been rewetted. The scanning curves show that this return takes place over the range of humidities 11 to 100% R.H. DTA will show that part of the water is returned below 11% R.H.

In comparing the two isotherms for preparations B and C it can be observed that the sorption boundary curve for B (d-dried) has a greater slope. To illustrate this, the latter is drawn on the same axis as the C preparation.

Preparation C contained approximately 3% more moisture than preparation B at the start of the isotherm, but this difference was regained completely by preparation B at higher humidities. This was apparent because both preparations had completely regained all the water lost after being exposed to 100% R.H. This lack of recovery at the low humidities of all the extra water removed explains the much larger hysteresis loop of preparation B (d-dried).

Several points may be taken from these results:

(a) The C preparation which was not d-dried did not allow complete regain of water when exposed at low or intermediate humidities, even after extended periods. This is explained by interlayer hysteresis described in the new model.

(b) If the BET calculations are applied to the boundary sorption curve of preparations B or C, results would be completely fictitious since interlayer water is re-entering in the 0-33% R.H. range. Values would be controlled by how the interlayer water re-entered the sample. Conclusive evidence that water enters in the BET region is derived from the scanning curves and the fact that preparation B (d-dried) has a steeper curve in that region. If the extra water removed from preparation B was solely physically adsorbed, it would have readsorbed below 10% R.H., where it was

removed. The increased steepness in the curve in the BET region is due to increased interlayer re-entry in this region.

A calculation for surface area could be made from the curve for the A preparation, since no interlayer water appears to be entering on this curve in the BET region. However, the position for zero adsorbed water is not known. Special procedures involving simultaneous measurement of sorption and length change can be used to determine this. They have been used by Helmuth (8) and referred to as the Bangham, Freundlich, Feldman and Sereda method. The surface area obtained by Helmuth for the curve equivalent to curve C was similar to the area obtained by N_2 adsorption.

(2) Differential Thermal Analysis

The samples used in this study were in some cases conditioned for longer periods at the various relative humidities. The times are also tabulated on Table I.

For preparation B and B(R) a thermogram is presented on Fig. 2 for every condition on the sorption boundary curve series (A) as well as for all the points returned to 11% R.H., i.e., the points on the scanning curve series (B) at a heating rate of $10^\circ\text{C}/\text{min}$. For series A it may be observed that two endothermic peaks with peak temperatures varying in the range 65-80 and $90-105^\circ\text{C}$ form and grow simultaneously with increasing humidity. It should be made clear here that these temperatures are not exactly definable and are known to vary to some extent depending on the experimental conditions. The peaks for the heating rate of $10^\circ\text{C}/\text{min}$ are very clearly recognizable although the baseline shifts greatly at this rate. Of the two peaks the $90-105^\circ\text{C}$ peak is larger up to 84% R.H.; at 11 and 32% R.H., the $65-80^\circ\text{C}$ peak is small, showing that in the region up to 11% R.H. most of the water sorbed is associated with the higher temperature peak.

Series B shows clearly how 11% R.H. on the sorption isotherm is not a uniquely defined point as also can be seen in Fig. 1, where the amount of water contained at 11% R.H. varies with the conditions of exposure. The higher temperature peak grows bigger as the relative humidity to which the

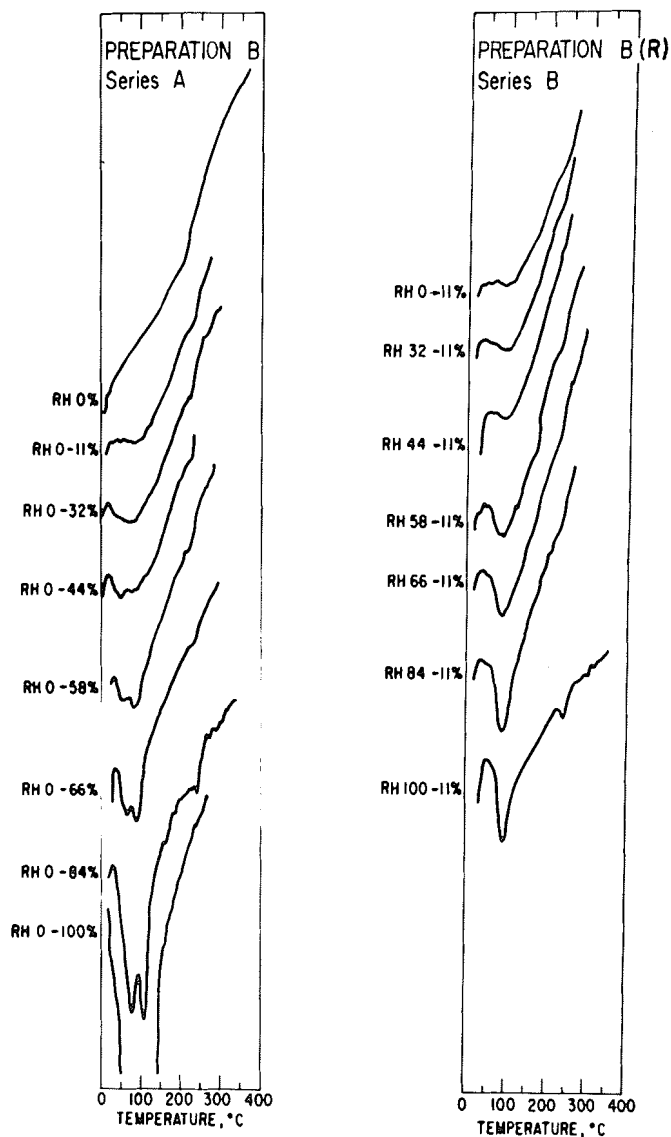


FIG. 2

DTA thermograms of preparation B and B(R)
 Series A - Preparation B equilibrated at R.H. of 0 to 100%;
 Series B - Preparation B(R) from R.H. of 0 to 100%,
 equilibrated at 11% R.H.

sample was exposed increases. The 65-80°C peak, on the other hand, is always reduced to a very small size on return to 11% R.H. Thus it is evident that the hysteresis effect manifested by the scanning curves observed on the sorption isotherm is associated with the high temperature peak. This hysteresis effect has been previously attributed to interlayer water

re-entry (2), and it is apparent that the two peaks distinguish between inter-layer water and water adsorbed on free surfaces.

The thermograms for preparations A, C(R) and C are presented on Fig. 3. Series A for preparation C(R) shows the curves for the samples that had been all returned to 11% R.H. after exposure to various humidities. It is clear that this preparation contained more water after drying than preparation B since an extended endothermal effect is visible below 100°C for the 0% R.H. curve. Subsequent exposure to higher humidities and back to 11% R.H. causes the 90-105°C peak to grow. The 65-80°C peak is small or not visible. This series is thus similar to that for preparation B. Series B, the samples exposed at different humidities shows, as for preparation B, a simultaneous growth of both peaks, the higher temperature peak not being surpassed in intensity by the lower temperature peak until 76% R.H.

Series C represents preparation A exposed to various relative humidities. This sample shows a well-developed peak at 90-105°C and a small peak at 65-80°C. As the relative humidity is raised the 65-80°C peak increases, surpassing the 90-105°C peak at 76% R.H. The latter appears to remain relatively constant, and the 65-80°C peak now appears to grow independently of the higher temperature peak. This explains the sorption curve for preparation A which has a very low slope in contrast to that of preparation B or C (Fig. 1). For preparation A all the water associated with the 90-105°C peak is already present, while for B and C it is sorbing as the humidity is increasing. The sorption hysteresis is explained also by this peak, and since preparation C has some of this water already present its hysteresis is not as large.

Comparing series B and C on Fig. 3, it appears that the lower temperature peak for C is larger for the same humidity. This may be due to a larger surface area of the undried sample. Some other experimental results confirming this have been obtained and will be published later.

Discussion

Despite the extraordinary lengths of time allowed for equilibrium at the various conditions described above these results are essentially the same

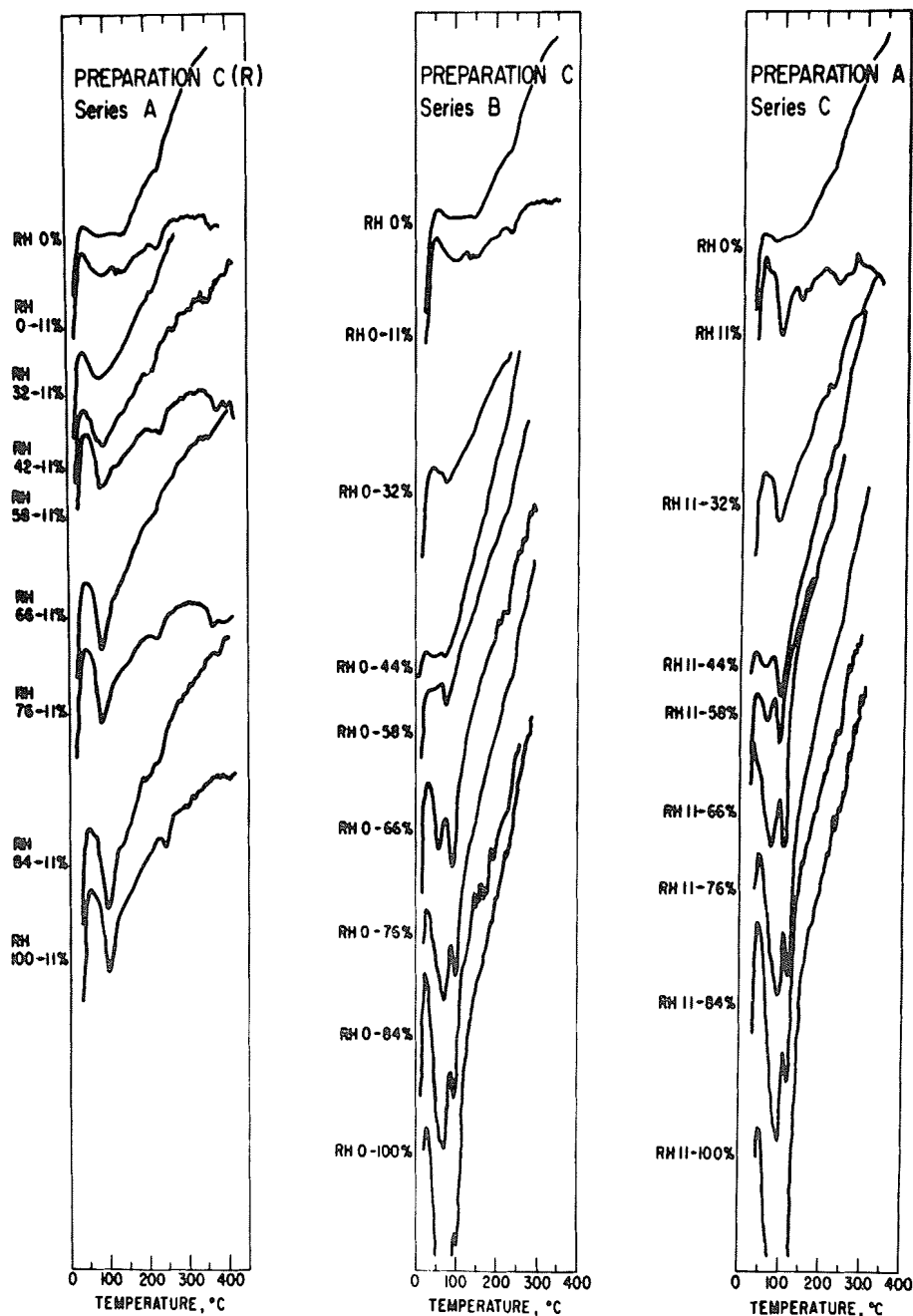


FIG. 3

DTA thermograms of preparations A, C(R) and C
 Series A - Preparation C(R) from R.H. of 0 to 100%,
 equilibrated at 11% R.H.

Series B - Preparation C equilibrated at R.H. of 0 to 100%.
 Series C - Preparation A equilibrated at R.H. of 0 to 100%.

as those obtained before when the equilibration periods were much less (2).

The results clearly show the following:

- (a) adsorption and desorption curves are well defined by the experimental points and a large hysteresis loop is confirmed;
- (b) scanning curves exist and are the result of re-entrance of interlayer water;
- (c) practically all water removed on first drying from 11% R.H. is regained by rewetting;
- (d) interlayer water re-enters throughout the BET range; thus conventional surface area calculations from water sorption are not valid.

In this paper it was possible to correlate the 90-105°C peak with interlayer water and thus it was possible to observe directly how the amount of interlayer water changes with humidity. Progressive re-entry of interlayer water into the d-dried material takes place in stages beginning with exposure at very low humidities and is not complete until it exceeds about 75% R.H. There seems to be a form of equilibrium at each humidity; this was discussed in an earlier paper (2). From the correlation of the 90-105°C peak with interlayer water and from preparation C, the partially dried preparation, it was possible to observe that interlayer water entered when the samples were exposed from the dry to 11% R.H. by a growth in the 90-105°C peak; this growth also occurred in the BET region.

The significance of the 11% humidity position is obvious in the thermograms. For an ideal adsorption system the amount adsorbed at 11% R.H. should be uniquely defined. At about 11% R.H. a monolayer usually exists without the complicating features of capillary condensation. Also in this region adsorption is expected to be reversible along the adsorption curve. However, in the cement system any number of positions exist between the upper and lower boundaries of the hysteresis loop. This is also evident from the peak intensities at 90-105°C in the thermograms. The 90-105°C peak in preparation A at 11% R.H. is similar to that in prepara-

tions B and C exposed to 84 or 100% R.H. and returned to 11% R.H. Exposure of preparation A to different humidities causes only peak 65-80°C to grow. An explanation based on the reasoning that the 90-105°C peak is due to the desorption of a monolayer of adsorbed water can be rejected for the following reasons.

- (1) When the peak is removed by drying it can only be restored by exposure to high humidities.
- (2) Samples can be prepared by exposure to different humidities and maintained at 11% R.H. even though they contain different amounts of water. This is also manifested by the 90-105°C peak being of different sizes. The 11% R.H. position is not unique. This situation is well explained by the new model of hydrated portland cement.
- (3) Thermal analysis of porous glass at different humidity conditions (6) shows that the monolayer cannot be differentiated from the multilayers.

The higher temperature peak is explained as due to the expulsion of interlayer water. This may not necessarily be due only to a higher energy of binding of these H_2O molecules over those physically adsorbed but also due to the mechanical barrier imposed on the interlayer water because of their interlayer positions. Although two peaks can be observed it is clear that there must be some overlap in the interaction energies.

Conclusions

Thermal analysis allows differentiation of interlayer and physically adsorbed water.

Different degrees of drying of samples and long periods allowed for equilibration support all sorption results on which the new model of hydrated portland cement is based.

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