NRC Publications Archive Archives des publications du CNRC

A datum point for estimating the absorbed water in hydrated Portland cement

Feldman, R. F.; Sereda, P. J.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1002/jctb.5010130902>

Journal of Applied Chemistry, 13, 9, pp. 375-382, 1963-11-01

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=bc3fee0b-d31d-4dbe-9200-dc51ca3307c2>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=bc3fee0b-d31d-4dbe-9200-dc51ca3307c2>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Ser
TH1
N21r2
no. 204
c. 2

BLDG

18557
ANALYZED

NATIONAL RESEARCH COUNCIL
CANADA

DIVISION OF BUILDING RESEARCH

A DATUM POINT FOR ESTIMATING THE
ADSORBED WATER IN HYDRATED PORTLAND CEMENT

BY

R. F. FELDMAN AND P. J. SEREDA

REPRINTED FROM
JOURNAL OF APPLIED CHEMISTRY, VOL. 13, 1963, P. 375-382

RESEARCH PAPER NO. 204
OF THE
DIVISION OF BUILDING RESEARCH

OTTAWA

PRICE 25 CENTS

NOVEMBER 1963

NRC 7560

This publication is being distributed by the Division of Building Research of the National Research Council. It should not be reproduced in whole or in part, without permission of the original publisher. The Division would be glad to be of assistance in obtaining such permission.

Publications of the Division of Building Research may be obtained by mailing the appropriate remittance, (a Bank, Express, or Post Office Money Order or a cheque made payable at par in Ottawa, to the Receiver General of Canada, credit National Research Council) to the National Research Council, Ottawa. Stamps are not acceptable.

A coupon system has been introduced to make payments for publications relatively simple. Coupons are available in denominations of 5, 25 and 50 cents, and may be obtained by making a remittance as indicated above. These coupons may be used for the purchase of all National Research Council publications including specifications of the Canadian Government Specifications Board.

Reprinted from the *Journal of Applied Chemistry*, 1963, Vol. 13, pp. 375—382

A DATUM POINT FOR ESTIMATING THE ADSORBED WATER IN HYDRATED PORTLAND CEMENT

By R. F. FELDMAN and P. J. SEREDA

In order that it may be possible to differentiate between adsorbed water and water chemically bound in hydrated Portland cement, a study was conducted of the dimensional-change sorption characteristics at low relative vapour pressures.

By use of compacts of bottle-hydrated cement fabricated at loads between 5000 and 65,000 lb., equilibrium as well as dynamic values were obtained for dimensional change and moisture change relationships below 20% R.H. The apparatus enabled experiments to be performed in high vacuum.

For the first rewetting and second drying it was found that for equilibrium points from 7.2 to 17.6 and 17.7 to 7.9% R.H. the plots of $(\Delta l/l)$ vs $(\Delta W/W)$ were both linear. After degassing the specimens beyond 7.9% R.H., the dynamic points continued along the straight line traced out by the equilibrium points in the plot mentioned and a sharp transition point was obtained. The vapour pressure in the region of this transition point, referred to as datum point, was less than 10μ . Further degassing produced another linear region.

It was concluded with supporting evidence from work on other porous materials that the datum point where the transition between the linear portions of the curve occurs, will yield a good estimate of the true value for adsorbed water and will thus approximate to the point for zero adsorbed water; it will also separate the processes of desorption and dehydration. This establishes therefore a method for determining the adsorbed water in hydrated cement.

The results obtained from the compacts of bottle-hydrated cement indicate that by this method the surface area, as calculated from the B.E.T. theory, will be considerably lower than that obtained from the high value for the evaporable water (determined by the method of Copeland & Hayes).

Introduction

Hydration products of Portland cement are described as ribbon-like fibres, plates and crumpled sheets, the substance being poorly crystallised and given the general name 'paste'. The chemically combined water in these hydrates, termed 'non-evaporable water' of amount ' W_n %',* can be partially withdrawn at very low vapour pressures¹ because of decomposition of the hydrates before all the physically adsorbed water has been removed from the surfaces of the microcrystalline material. Thus during drying at 21° , the removal of the sorbed water merges into the removal of the chemically bound water so that it is difficult to distinguish between the two.

Since the knowledge of W_n is essential to the study of the chemical and physical properties of the paste, arbitrary conditions of drying were established which defined the point when practically all adsorbed water was removed. Powers & Brownyard^{2,3} have determined W_n after drying the hardened cement paste in a vacuum system containing magnesium perchlorate dihydrate and tetrahydrate, whereas Copeland & Hayes⁴ used a dry-ice trap to establish the water-vapour pressure. In these methods, however, the paste does not reach constant weight; rather, a constant rate of loss of weight is attained. Copeland & Bragg⁵ state, however, that non-evaporable water in specimens dried by the procedure of Copeland & Hayes probably corresponds rather closely to chemically combined water.

Once the drying procedure for Portland cement paste had been established, the theory of Brunauer, Emmett & Teller⁶ was applied by many workers.^{2,7-11} This application of the theory is still in constant use, and has proved to be a valuable tool for studying the physical structure. This work largely provided the information by which it is now understood that the products of cement hydration consist of submicroscopic crystals which form a stiff colloidal gel. Nitrogen sorption^{9,12} as well as other evidence^{13,14} have also demonstrated this.

There is considerable controversy, however, regarding the values obtained for the surface area of paste because there is a difference between the values obtained by nitrogen sorption and those obtained when water is used as sorbate. Even values obtained with water differ considerably depending on the history of the sample.¹¹ The uncertainty in the determination of W_n , and V_m (the parameter in the B.E.T. equation from which a value for specific surface is calculated), caused by the somewhat arbitrary definition of the dry state may be contributing to some of the variations noted above. For this reason, it would be a great advance to find an absolute method for determining V_m and W_n .

Studies on other porous materials¹⁵⁻¹⁷ have shown that a knowledge of the relationship between dimensional change and moisture content provides valuable information for the study

* W_n is defined as the quantity of water retained by the hydrated paste when dried to constant weight through a dry-ice trap.

of the process of adsorption and of the physical characteristics of these porous materials. Work by the present authors¹⁸ on other hydrous porous systems, notably $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, has shown that combined measurements of water uptake or loss and corresponding dimensional changes can be used to differentiate between the sorbed water and the chemically bound water, because the dimensional change due to unit change of chemically bound water content is usually different from the dimensional change due to unit change in adsorbed water content.

Although experimental results of the shrinkage of hydrated paste¹⁹⁻²² have served to explain certain practical problems, the drying conditions have not been defined sufficiently accurately, nor measurements made precise enough to enable the use of the results in analyses or interpretations of the phenomenon. Even reports of results of equilibrium measurements of shrinkage as a function of the water loss²³⁻²⁶ do not differentiate between the different types of water because most of the measurements were not extended below 30% R.H.

The present work was done to provide precise equilibrium information below 20% R.H. for dimensional-change-moisture-change relationships of hydrated Portland cement paste with a view to differentiating between the adsorbed and non-evaporable water content.

Experimental

To obtain precise measurements of the changes in water content at given conditions of vapour pressure and the corresponding dimensional changes, it was desirable to use rigid samples of hydrated Portland cement paste which would have a well-defined and reproducible total pore system. In addition, the samples should be very thin to allow a short time to equilibrium and to minimise gradients of moisture content which may affect dimensional change measurements. Finally, it was desirable to have the cement completely hydrated. A sample of polyethylene bottle-hydrated cement paste²⁷ was obtained from the Portland Cement Association laboratories which was considered completely hydrated. (Experience in the study of cement hydration is that cements with W_n of 23–25% are almost completely hydrated.) Information concerning the composition of the clinker and its calculated potential composition has been published.²⁸ It has been designated as No. 18 and is a Type I cement.

After the cement had been dehydrated in a polyethylene bottle on a rotating wheel at water/cement ratio (W/C) of 5 for 90 days, it was dried over calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 11% R.H.) and stored. The hydrated cement was in powdered form. The non-evaporable water in this paste, determined by ignition at 1050° after drying at 105°, was found to be approx. 23% as compared with the value 21.7% obtained by hydrating the cement at a W/C ratio of 0.4 for 1 year.

Compacts made from this powdered paste of particle size less than $1\ \mu$ were formed in a range of porosities by varying the pressure at which the samples were compacted. Compacts in the form of discs of about $\frac{1}{16}$ in. thickness were compacted in a mould 1.250 in. in diameter. Loads of from 5000 to 65,000 lb. were applied to the pistons to form the compacts of different porosities. Hereafter the symbol 'L' will represent 1000 lb. load on a piston of 1.250 in. diameter. Thus a compact designated as 5L represents one compacted at 5000 lb. Previous work on compacts made from a variety of powders^{17,18} has shown that the dimensional changes of a compact during sorption give a true representation of a rigid porous system. Results of this work substantiate the belief that compacts of hydrated Portland cement also give a true representation of a rigid system defined by the geometry and size of the particles and their spacing. It is not known, however, whether the pore system of a compact of a given equivalent W_e/C ratio* is truly representative of paste hydrated from a mix of the same W/C ratio. Work in progress is attempting to clarify this question.

Apparatus

The high-vacuum apparatus used for this work was designed to expose 12 samples simultaneously for long periods to the same vapour pressure conditions, with exclusion of air. Six of these samples were mounted in individual tubes on quartz spirals of the McBain-Bakr type giving the results of the weight changes to a sensitivity of 2.6×10^{-5} g. The remaining six samples were mounted on modified Tuckerman optical extensometers and placed in individual cells equipped with optical windows.²⁹ This yielded the dimensional changes with changes in

* W_e/C the equivalent water-cement ratio of the compact, is defined as the W/C of normally hydrated cement which will produce on approximately complete hydration the same total pore volume as that of the compact of bottle-hydrated cement. This is calculated by use of the density of hydrated cement as 2.67 g./c.c. and of unhydrated cement as 3.0 g./c.c. The volume of gel pores is taken as 26% by volume of the gel system.

vapour pressure to a sensitivity of 2×10^{-6} in./in.

A three-stage oil diffusion pump backed by a rotary vacuum pump was used to obtain pressures of 10^{-6} mm. Hg.

The adsorbate was introduced into the system from a bulb which was immersed in a bath that could be controlled at temperatures between 0° to 70°F to within $\pm 0.1^{\circ}\text{F}$. The samples were maintained at 70°F by immersing the lower ends of the tubes and cells containing the samples to a depth of 12 in. in a controlled bath. Room temperature was controlled at $73 \pm 1^{\circ}\text{F}$.

Procedure

Two samples measuring about $1\frac{1}{8} \times \frac{3}{8} \times \frac{1}{16}$ in. were cut from each compact and mounted, one on the extensometer and the other on the quartz spiral. Initial degassing of these samples (referred to below as 'first drying') was achieved by evacuating simultaneously through a manifold. A dry-ice trap was used together with three-stage diffusion and rotary pumps; degassing continued for as long as 8 days.

Adsorption was achieved by allowing the manifold to attain a humidity of 7.2% by control of the temperature of the bath in which the water source was immersed, and exposing the samples simultaneously to this humidity. This procedure was continued for equilibrium points up to 17.6% humidity. Three days were allowed for equilibrium to be attained between points and 15 h. of constant weight always elapsed before the system was considered to be in equilibrium. The samples were then taken to saturation and redried to 17.7% and four equilibrium points were again obtained between 17.7 and 7.9% humidity. The samples were then dried in pairs by evacuation, those that had been made at the same pressure, simultaneously, one on a spiral and the other on the extensometer. Dimensional-change and weight-change measurements were taken continuously. (Humidity in this paragraph is R.H.).

Results

(1) First drying (from 11% R.H.)

Fig. 1 shows the weight loss-time curves for the 5L to 55L compacts and also for a powdered sample. It is seen that the rate of weight loss is greatest for the powdered material and decreases considerably the higher is the fabrication pressure of the compact. These curves demonstrate how the porosity of the sample can affect the rate of water loss during drying by evacuation through a dry-ice bath. Thus different amounts of total water can be removed from different samples even though they all may be dried until they reach the point when they lose water at the same rate of 1 mg. per g. of sample per day which was arbitrarily set as the point when the evaporable water has been removed. These results show that the criterion for determining the evaporable water cannot be used for compacts as the sample must be ground to a fine particle size.⁴ The evaporable water was determined for the powdered material and, as shown in Fig. 1, is not far removed from that of the 5L compact.

Fig. 1. Plots showing the rate of moisture loss from compacts of hydrated cement during drying by evacuation through dry-ice trap

● 5L ○ 15L ▲ 30L △ 45L ■ 55L □ powder

Fig. 2 shows a plot of the length change vs the weight loss which yields straight lines for all the compacts made at the different pressures; the greater the load for compaction, the steeper is the slope of these curves. This plot also shows that if the straight lines are extrapolated they will not pass through the point representing the state of the compacts before drying from 11.0 R.H. In order to pass through this point, a break in the straight line, i.e. a change in slope, is anticipated.

Fig. 2. Plot of contraction vs weight loss during first drying of compacts of hydrated cement

● 5L ○ 15L ▲ 30L △ 45L ■ 55L □ 65L

It is significant that despite the obvious differences in the permeability of the samples (the 5L compacts have quite a high porosity compared with the 65L compacts, see Table I), all the compacts give the same general results: straight lines which do not extend through the starting point. These values were obtained over a period of 8 days, during which time the rate of weight loss was very slow. It can be concluded that little or no moisture gradients existed through the samples and that the values represented on Fig. 2 are well defined, although the equivalent equilibrium relative humidities were not known. It is known, however, that these humidities were well below 7.5%.

(2) First rewetting

The equilibrium points for the first rewetting between 7.2 and 17.6% R.H. show a linear plot for the dimensional change vs change in moisture content. If this linear plot is extrapolated back, it is seen that to pass through the starting point for rewetting a change in slope has to occur. These results are shown in Figs. 3 and 4 for the 5L and 45L compacts respectively. Both these plots are considerably below their respective first drying curves.

Table I

Physical characteristics of compacts of bottle-hydrated cement and its water content at 17.7% R.H. relative to datum point

Load, lb.	5L	15L	30L	45L	55L	65L	Powder
Porosity, % void fraction	63.5	51.1	42.9	39.5	35.8	33.8	—
Equivalent W/C ratio	0.926	0.713	0.581	0.505	0.467	0.436	—
% water* from datum point to 17.7% R.H.							
1st Rewetting	2.19	2.34	2.30	2.09	2.11	2.07	—
2nd Drying	1.96	1.99	1.95	2.10	1.77	1.80	—
% water† for 1st drying from 11% R.H.	4.68	4.56	4.27	4.19	3.97	4.13	5.11
% water† for 1st rewetting from driest point to 17.6% R.H.	3.72	3.65	3.48	3.30	3.13	3.07	4.42

* based on weight at datum point

† based on weight at driest point

Fig. 3. Plot of length change vs moisture content change for 5L compact of hydrated cement

- △ first drying (dynamic points)
- ▲ second drying (dynamic points)
- first rewetting (equilibrium points)
- second drying (equilibrium points)

(3) Second drying curve

All the samples were taken to approximately saturation conditions and then redried to 17.7% R.H.; four equilibrium points were taken down to 7.9% R.H. The ($\Delta l/l$) vs ($\Delta W/W$) plot is again linear, the plot for the 5L compact being slightly above its first wetting curve and the 45L compact somewhat below the first wetting curve. The significance of this will not be discussed here, suffice it to say that it is considered to be in line with accepted ideas of drying shrinkage.

At the stage after 7.9% R.H., further drying was effected by continuous pumping. The curve for both plots (Figs. 3 and 4) continues to follow closely the straight line traced out by the previous equilibrium points. At a certain point these straight lines showed an abrupt change in

Fig. 4. Plot of length change vs moisture content change for 45L compact of hydrated cement

- △ first drying (dynamic points)
- ▲ second drying (dynamic points)
- first rewetting (equilibrium points)
- second drying (equilibrium points)

slope and continued along a new linear curve of steeper slope. It was found that the change in slope was more abrupt for the compacts formed at the higher pressures than the ones at the lower. This is typified in Figs. 3 and 4. It was also observed that the slopes of these linear portions seem to decrease with the repeating cycles of wetting and drying.

The above experiment, where drying below 7.9% R.H. was effected by continuous pumping, was repeated on another sample; here, however, pumping was carried out for short periods, followed by long intervals of up to 15 h. to attain equilibrium. It was found that the results of the two experiments did not differ. Shortly after the abrupt change in slope on the $(\Delta l/l)$ vs $(\Delta W/W)$ plot, pumping was terminated and the sample was allowed to reach equilibrium within the sorption system for 4 days. Manometer measurements indicate that the equilibrium vapour pressure is less than 30μ and computations from the knowledge of sample weight loss and dead space of the apparatus using the gas laws show that the vapour pressure is less than 10μ .

Discussion

A sharp break in the $(\Delta l/l)$ vs $(\Delta W/W)$ curve was discovered in this second drying curve, and served as the boundary between two linear portions. The same plot for other adsorbents with water as adsorbate, Vycor glass,¹⁶ precipitated calcium carbonate, and 'Cab-O-Sil' silica,¹⁷ which is a form of silica in the particle size range 0.01 – 0.03μ , shows a linear portion through the origin, i.e. zero adsorbed water and zero expansion, and extending to one or two molecular layers of adsorbed water. This linearity also occurs for $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ before dehydration of the sample takes place at low pressures.¹⁸ As these cement compacts also show this characteristic down to low humidities, and then show a sharp break after some period of evacuation, it is considered that, in the transition region between the two linear portions of the curve, the point representing the onset of dehydration of the cement exists. This point is referred to henceforth as the 'datum point'.

Since the free-energy change of the surface on sorption can be expressed in terms of the dimensional change,¹⁵ it is expected that the processes of sorption and hydration should yield different $(\Delta l/l)$ vs $(\Delta W/W)$ relationships. It is possible that during evacuation, both processes—dehydration and desorption—may take place simultaneously. This, however, appears not to be the case for the first period of evacuation where the points obtained dynamically on the $(\Delta W/W)$ vs $(\Delta l/l)$ plot follow precisely the straight line formed by the equilibrium points. In Figs. 3 and 4, assuming that line EF represents the desorption process and line FG represents the dehydration process and possibly the continuing desorption process, the intersection of these lines represents the datum point. As shown in Figs. 3 and 4, however, line FG remains linear for the full range of observations. It is expected that the dehydration process alone will provide a linear $(\Delta l/l)$ vs $(\Delta W/W)$ relationship, and thus the linear curve FG can only represent two possible cases:

- (i) Hydrate water alone is being removed along line FG; some adsorbed water remains, this being the amount in equilibrium with the vapour pressure at which the cement is dehydrating.
- (ii) The hydrate water and adsorbed water are being removed simultaneously in the same proportions.

The probability of the latter case is considered remote; as adsorbed water is removed, the greater will be the adsorption energy of the remaining water. Further, the vapour pressure in this region is in the order of a few microns, and the amount of adsorbed water remaining will be very small. From these considerations the first case is favoured with F representing the point above which no hydration water can be removed and below which the amount of adsorbed water remaining is necessarily small. This datum point yields a value for adsorbed water closely approximating the true value.

The slight deviation of the actual points in this transition regions shows that the two processes do take place simultaneously for a short period. The degree of deviation is greater for the 5L compact, however, than for the 45L compact and it is almost negligible for the latter. This can be well understood when one considers the permeabilities of the respective samples. Evacuation for 50 min. is required for the 5L compact before the datum point is reached from the last equilibrium point, while 110 min. are required for the 45L compact. Because of this, there is more chance of the two processes, desorption and dehydration, occurring separately for the 45L compact, and thus for that sample the transition region is sharper.

In Figs. 3 and 4, line BC was constructed by drawing a line parallel to GF and through B, the point reached for the first drying. Where BC intersects DC, the first rewetting curve, at C, is

considered to approximate the datum point. When considering the reverse process of adsorption, BC represents the hypothetical rehydration curve. This shows that the datum points in Figs. 3 and 4 for the first rewetting and second drying curves are considerably displaced. Study of the equilibrium data of weight change to relative humidity from 0 to 17.6% for both first rewetting and second drying (Fig. 5), using the respective datum points as the points for zero adsorbed water shows that the whole curve for drying (desorption) lies considerably above that for rewetting (adsorption) and that the difference between the zero point and 17.6% R.H. for both cases is very similar. It is now seen (Fig. 5) that the equilibrium curves for adsorption and desorption are separate, the position in terms of the moisture content at similar relative humidities being that the desorption value is much higher than the adsorption value. The full significance of this fact is being investigated more thoroughly.

Fig. 5. Plot of weight change vs relative vapour pressure for compacts of hydrated cement

● second drying ○ first rewetting
(a) compact 5L (b) compact 45L

Table I shows the values obtained in terms of weight per cent, using the weight of the sample at the datum point in each case as the dry weight of the sample. These quantities are for the change in weight ($\Delta W/W$) from the datum point to 17.7% R.H. humidity. For the first rewetting the average for the six pressures of fabrication is 2.18% and for the second drying 1.94%. There is a decrease in this value from 2.18 to 1.94% from first rewetting to second drying. This is probably due to a decrease in area as shown by Tomes *et al.*¹⁰ on cycling experiments. The similarity between the above values for all pressures of fabrication, despite the great change in the total porosity of the compact with pressure of fabrication (Table I) or equivalent W_e/C ratio, indicates that these results are not affected by moisture gradients that might have occurred during evacuation when the dynamic points were obtained.

Comparison of the data obtained by Lerch *et al.*²⁸ for the same cement (Table II) (results recalculated as % of dry paste through knowledge of W_n), shows that for a one-year hydrated cement at W/C ratio of 0.4, the sorbed water at 36% R.H. is 5.8%. This means that, at 17.7% R.H., the sorbed water would be approximately 4.1% by weight of the dry paste or 70% of sorbed water at 36% R.H. This is considerably higher than the 2.18% obtained in this work. It is possible, however, that the bottle-hydrated cement does not have the same morphology and surface area as the cement hydrated in the normal manner.

By use of these compacted samples, the comparison of results obtained by measuring the sorbed water from the datum point to 17.7% R.H. (new method) with those obtained by the conventional method of degassing until a weight loss of less than 1 mg./g. of sample per day is recorded, shows that values obtained by the new method are much lower than those obtained for either the first drying or the first rewetting by the conventional method.

Table II

Conventional method of determination²⁸ of physical characteristics
(Non-evaporable water % for W/C of 0.4)

Time	7 days	28 days	3 months	1 year
% *	16.2	19.2	20.9	21.7
Sorption at 0.36† P/P_0 , %	4.0	5.3	6.0	5.8
Approximate sorption† at 17.7% R.H., %	2.8	3.7	4.2	4.1

* based on weight of original unhydrated cement

† based on weight of dry hydrated cement

Conclusion

A new method for differentiating between adsorbed and non-evaporable water has been developed. By plotting dimensional changes against weight change, two distinct linear portions are obtained in the curve. It is concluded, with supporting evidence from work on other porous materials, that the point where the transition between the linear portions of the curve occurs is here defined as the datum point for zero adsorbed water. It then appears that this is a method for determining the adsorbed water in a compact of hydrated cement. The values obtained by the conventional method of drying differ greatly from compact 5L to 65L, although the value for the powdered sample does not differ much from the 5L compact. The values obtained by the new method are practically independent of pressure and are much less than the values obtained for either the first drying or the first rewetting by the method of Copeland & Hayes.⁴ This means that the surface area as calculated from the B.E.T. theory will be much less than that obtained when the high value for the evaporable water (as determined by the Copeland & Hayes method) is used.

A further comparison shows that the values obtained for bottle-hydrated cement by the new method is much less than that obtained by conventional methods⁴ for samples of the same cement hydrated at W/C of 0.4 in the normal manner, although the W_n is greater for the bottle-hydrated cement than the cement hydrated normally for a year. It is possible, however, that the bottle-hydrated cement does not have the same morphology and surface area as the cement hydrated in the normal manner.

Acknowledgments

The authors are grateful to Mr. N. R. Greening of the Portland Cement Association who supplied the sample of bottle-hydrated Portland cement. They also wish to acknowledge the valuable assistance of H. F. Slade and S. E. Dods in setting up the apparatus and recording the information. This paper is a contribution from the Division of Building Research, National Research Council, Canada, and is published with the approval of the Director of the Division.

Division of Building Research,
National Research Council,
Ottawa 2,
Canada

Received 18 March, 1963

References

- Brunauer, S., Copeland, L. E., & Bragg, R. H., *J. phys. Chem.*, 1956, **60**, (1/2), 112
- Powers, T. C., & Brownyard, T. L., *Proc. Amer. Concrete Inst.*, 1947, **43**, 101, 249, 469, 549, 669, 845, 865, 933, 971
- Powers, T. C., *Bull. Amer. Soc. Test. Mat.*, 1949, No. 158, 68
- Copeland, L. E., & Hayes, J. C., *Bull. Amer. Soc. Test. Mat.*, 1953, No. 194, 70
- Copeland, L. E., & Bragg, R. H., *Bull. Amer. Soc. Test. Mat.*, 1955, No. 204, 34
- Brunauer, S., 'The adsorption of gases and vapours', 1943, Vol. I (Princeton Univ. Press)
- Jesser, L., *Zement*, 1927, **16**, 741
- Giertz-Hedstrom, S., *Proc. Symp. Chemistry of Cements* (Stockholm), 1938, p. 505
- Gleysteen, L. F., & Kalousek, G. L., *Proc. Amer. Concrete Inst.*, 1955, **51**, 437
- Tomes, L. A., Hunt, C. M., & Blaine, R. L., *J. Res. nat. Bur. Stand., Wash.*, 1957, **59**, 357
- Hunt, C. M., Tomes, L. A., & Blaine, R. L., *J. Res. nat. Bur. Stand. Wash.*, 1960, **64A**, 163
- Blaine, R. L., & Valis, H. J., *J. Res. nat. Bur. Stand. Wash.*, 1949, **42**, 257—267
- Bernal, J. D., 'Structures of cement hydration compounds', *Proc. 3rd Int. Symp. Chemistry of Cement* (London), 1952, p. 222
- Swerdlow, M., McMurdie, H. F., & Heckman, F. A., *Proc. Int. Conf. Electron Microscopy* (London), 1954, p. 500
- Bangham, D. H., & Maggs, F. A. P., *Proc. Conf. on the ultra-fine structure of coals and cokes* (British Coal Utilization Res. Ass.), June 1943, p. 118
- Amberg, C. H., & MacIntosh, R., *Canad. J. Chem.*, 1952, **30**, 1012
- Sereda, P. J., & Feldman, R. F., *J. appl. Chem.*, 1963, **13**, 150
- Feldman, R. F., & Sereda, P. J., *J. appl. Chem.*, 1963, **13**, 158
- Menzel, C. A., *Proc. Amer. Concrete Inst.*, 1935, **31**, 125
- Carlson, R. W., *Proc. Amer. Soc. Test. Mat.*, 1935, **35**, 370
- Pickett, G., *Proc. Amer. Concrete Inst.*, 1956, **52**, 581
- Alexander, K. M., & Wardlaw, J., *Aust. appl. Sci.*, 1959, **10**, 201
- Dutron, R., *Ann. Trav. publ. Belg.*, 1934, **35**, 243, 347
- Haller, P., Eidg. Mat. Prüf. Anstalt (E.M.P.A.), Zürich, Diskussionsber., 1940, No. 124
- Powers, T. C., *J. Amer. ceramic Soc.*, 1958, **41**, (1), 1
- Kalousek, G. L., *Amer. Concrete Inst.*, 1954, **26**, 233
- Brunauer, S., Kantro, D. L., & Copeland, L. E., *J. Amer. chem. Soc.*, 1958, **80**, 761
- Lerch, W., & Ford, C. L., *Proc. Amer. Concrete Inst.*, 1948, **44**, 745
- Feldman, R. F., & Sereda, P. J., *Proc. Amer. Concrete Inst.*, 1961, **58**, 203

J. appl. Chem., 13, September, 1963