

# Dimensional Change and Water Sorption Studies Of Cement Paste

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Experimental data are presented which indicate that it is possible to differentiate between various types of water lost by cement paste during drying. Results include the relationship between weight loss and shrinkage and their relationship to the heat of desorption.

●CEMENT PASTE exhibits the characteristic of swelling and shrinking in response to variations in relative humidity. Although the relationship between the dimensional change and the amount of water held by the paste has been studied by many workers, not all the phenomena have yet been adequately explained. Often the relationship between water loss and drying shrinkage is represented by a continuous curve with no evidence of breaks, but Alexander and Wardlaw (1), using a dynamic method of drying specimens, established that at least one break occurred. Verbeck's work reviewed in the Yearly Report of the Portland Cement Association (2) also indicated a break in the shrinkage/weight-loss curve. In a recent publication Verbeck (3) concluded that two different types of water are desorbed from cement paste, each type having a constant shrinkage/water-loss ratio over its operative range. Moreover, the two types of water had different heats of adsorption, yet each had a constant differential heat of adsorption over the entire range of water contents in which it operated. Powers (4) published a figure which suggested a complex relationship between the relative humidity and the dimensional changes. Recent studies by Feldman and Sereda (5, 6) on cement paste and hydrated cement compacts indicate that the relationship between dimensional change and water vapor pressures may further aid the elucidation of the cement paste structure. This paper describes experiments designed to provide further comprehensive data on shrinkage behavior of cement pastes.

## MATERIALS, APPARATUS AND PROCEDURE

### Shrinkage/Weight-Loss Relationship

Cement paste specimens, having dimensions of  $\frac{1}{4}$  by  $\frac{1}{4}$  by 6 in. and water/cement ratios of 0.35 and 0.50, were cast. After seven days curing in saturated air the bars were placed in controlled, CO<sub>2</sub>-free atmospheres having progressively lower relative vapor pressures (p/p<sub>o</sub>). \*\* The bars were brought to equilibrium with the water vapor in each atmosphere before being measured, weighed and exposed to a dryer condition. Vapor pressures were controlled by means of sulfuric acid-water mixtures.

### Relationship Between Shrinkage, Weight Loss and Heats of Desorption

Data for heats of solution were obtained on a mature cement paste using the method of Woods, Steinour and Starke (7). The cement paste had a water/cement ratio of 0.35, and was cured under water for 6 years. Carefully ground samples of the paste were

\*The experimental results presented in this report include work which was started at Portland Cement Association Laboratories, Skokie, Illinois, continued at the National Building Research Institute of the CSIR, Pretoria, South Africa, and is now being continued at CSIRO, Division of Applied Mineralogy, Melbourne, Australia.

\*\*The term p/p<sub>o</sub> used herein is usually written p/p<sub>o</sub>.

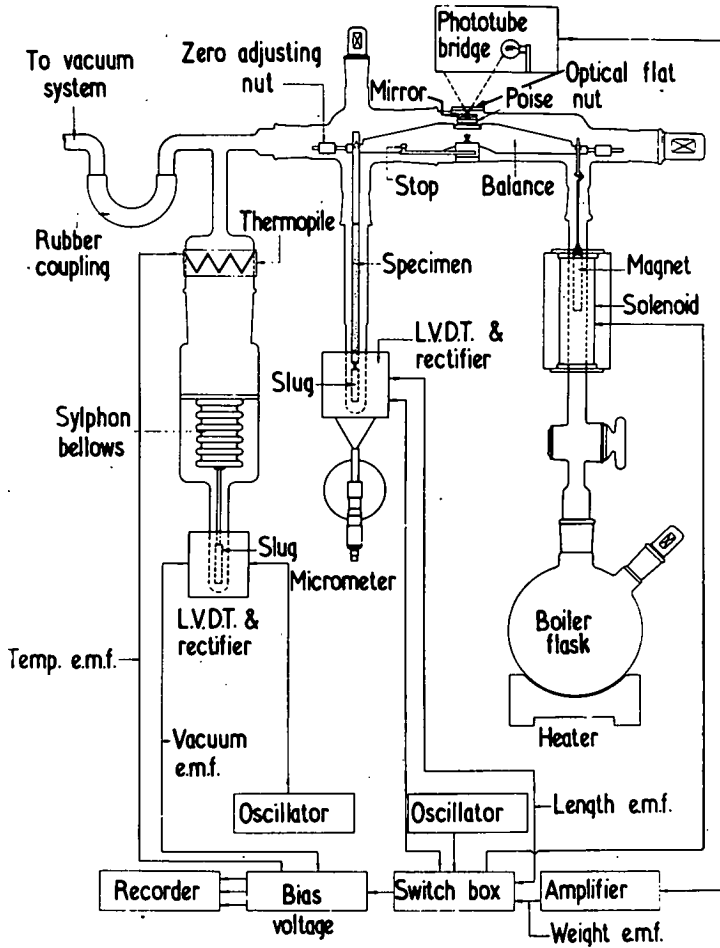


Figure 1. The recording sorption balance and extensometer.

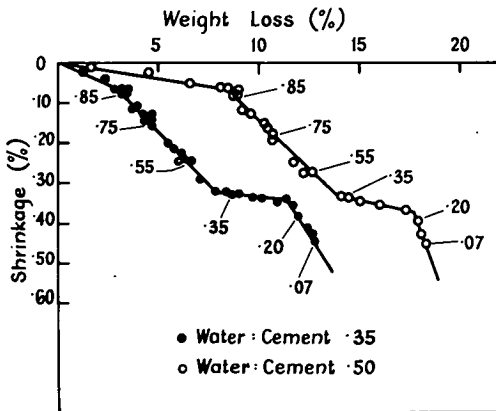


Figure 2. Relationship between weight loss and shrinkage at designated relative vapor pressures.

placed in sealed containers in which the atmospheres were maintained at various relative water vapor pressures. One sample was desiccated by means of a vacuum pump using a dry ice-alcohol trap, providing data for  $p/p_o = 0$ . When equilibrium was reached the specimens were sealed, weighed and immediately tested.

Specimens measuring  $\frac{1}{4}$  by  $\frac{1}{4}$  by 5 in. were cut from bars of the same cement and measured to determine shrinkage at various humidities.

#### Shrinkage/Weight-Loss Relationship Using Sorption Balance and Extensometer

An apparatus (Fig. 1) designed by Roper and Bryden (8), was used to

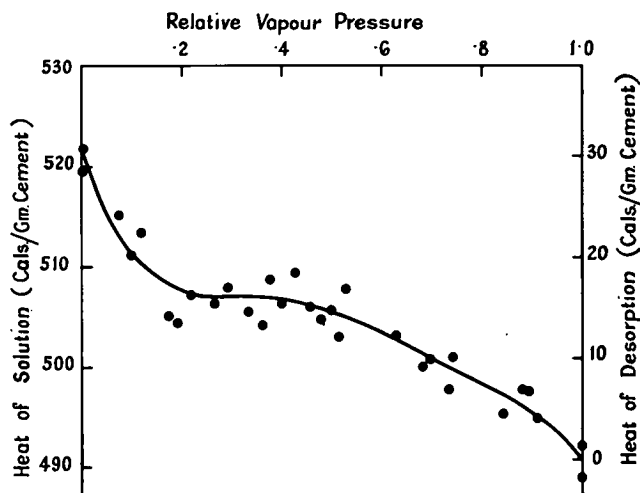


Figure 3. Relationship between heat of solution and relative vapor pressure with which the cement paste is in equilibrium.

measure both weight and length changes of bars in a controlled vapor pressure system where water vapor was the only gas in contact with the specimen. The temperature and vapor pressure in the system, and the changes in weight and length of the cement paste specimen, were measured automatically and recorded by a strip chart recorder. Measurements were made on two cement paste bars of different size; bar 1 was  $\frac{1}{4}$  by  $\frac{1}{8}$  by 5 in. and bar 2 was  $\frac{1}{4}$  by  $\frac{1}{4}$  by 5 in. Both bars had initial water/cement ratios of 0.33 and were moist cured for one day before being placed under water at 20 C. Bar 1 was tested after 28 days and bar 2 after 180 days curing. In both cases the bars were placed in the apparatus while still completely wet, and the air was then flushed from the system by boiling water in the flask (Fig. 1) under slightly reduced pressure. The water in the flask, which was at a temperature of about 60 C, provided most of the flushing vapor and loss of water from the bar, which remained at 20 C, is considered negligible. Slow pumping was continued for 15 min to insure that air was completely removed from the system.

At this stage the boiler flask was disconnected and the water vapor was pumped from the system in small amounts, the vapor pressure being checked after each pumping period. Further pumping removed the condensed water from the glassware and the first drop in the observed pressure was noted. At this point measurements of the equilibrium vapor pressure and length and weight changes commenced. Decrements in the vapor pressure were made as small as possible to allow the maximum number of points to be obtained. Desorption measurements on bar 1 were made until the relative vapor pressure was reduced to 0.05. Bar 2 was subjected to a desorption cycle down to  $p/p_0 = 0.05$ , followed by an adsorption cycle and finally by part of a second desorption cycle. Equilibrium between the bars and the prevailing relative vapor pressure was attained within 24 hr except when the relative vapor pressure was close to unity. This period was shorter than found necessary in other investigations because small specimens were used, very small changes were made in the vapor pressure, and water vapor was the only gas present in the system. The dimensional and weight change data were expressed as percentages, the total change from the saturated vapor pressure to  $p/p_0 = 0.05$  being taken as 100 percent. This permits easy comparison of the results.

## RESULTS AND DISCUSSION

### Shrinkage/Weight-Loss Relationship

The shrinkage/weight-loss curves of the cement bars are presented in Figure 2. Equilibrium points are labeled with the corresponding  $p/p_0$  value. Unlabeled points are

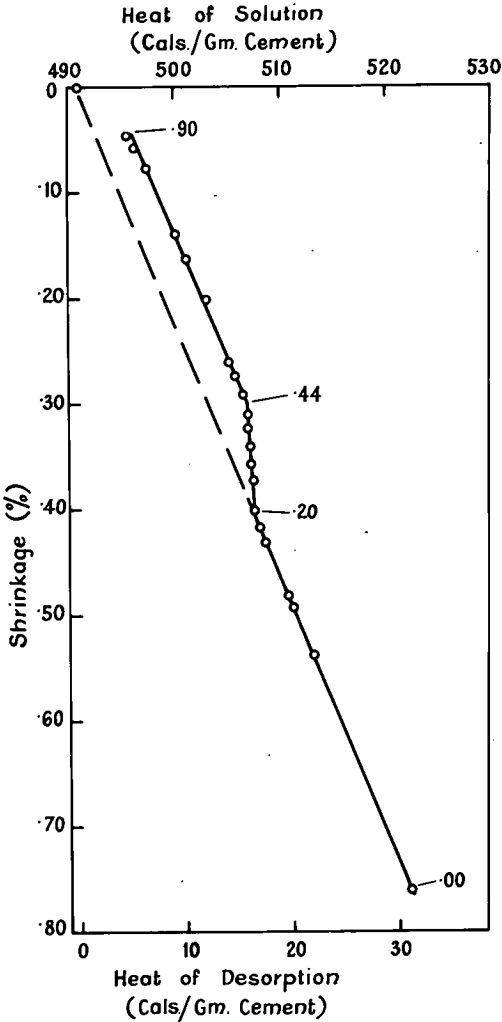


Figure 4. Relationship between heats of solution and shrinkage at designated relative vapor pressures.

those obtained when the bar has not yet attained equilibrium with the surrounding atmosphere, but from the viewpoint of shrinkage/weight-loss ratios they may be considered equilibrium points. The curves consist of four sections of differing slope, each of which is well represented by a straight line. It may be seen from Figure 2 that at the commencement of desorption a fairly large weight loss is accompanied by only a small amount of shrinkage, particularly in the case of the 0.5 water/cement ratio bars. Water of this type is apparently all removed before a  $p/p_o$  value of 0.85 is attained. The second type of water is more important from the shrinkage viewpoint and is lost within  $0.90 > p/p_o > 0.40$ . Within this range a substantial proportion of the entire shrinkage occurs. A third type of water is lost within approximately  $0.40 > p/p_o > 0.20$ . Its removal from the paste is accompanied by almost no shrinkage of the bars. Finally the removal of the fourth type of water takes place and between  $0.20 > p/p_o > 0$  the slope of the shrinkage/weight-loss curve is at its maximum.

It is concluded that the first type of water is that lost from the macropores of the cement paste. The loss of this water plays little part in shrinkage since the forces involved are small. The second type of water is that held by capillary condensation in the paste. The shrinkage associated with the loss of this water between  $0.90 > p/p_o > 0.40$  is thus due to capillary-tension stress. The third type of water, which is lost between  $0.40 > p/p_o > 0.20$  and is accompanied by almost no shrinkage of the bars, is considered to be associated with the destruction of concave menisci as proposed for similar materials (6, 9). Finally the remaining evaporable water consists of both adsorbed and hydrate water.

#### Relationship Between Shrinkage, Weight Loss and Heat of Desorption

Since a significant scatter occurs in the heats of solution values, a polynomial was fitted to the data by a least squares method. The resulting curve, together with the experimental points, is given in Figure 3. The difference between any value and the value  $p/p_o = 1.0$  is designated the heat of desorption. Within  $0.20 < p/p_o < 0.45$  very little change takes place in the heat of desorption curve despite that fact that water is lost from the paste over this interval. This is in contrast with the steep slope of the curve close to  $p/p_o = 0$ . The total heat of desorption, 31.1 cal/gm, compares favorably with the heat of adsorption as determined by Powers and Brownard (10) and quoted by Verbeck (3), namely 30.4, 30.8 and 30.9 cal/gm.

Using observed shrinkages and weight losses and plotting these values as functions of the calculated heat of adsorption, Figures 4 and 5 are obtained. It can be seen in

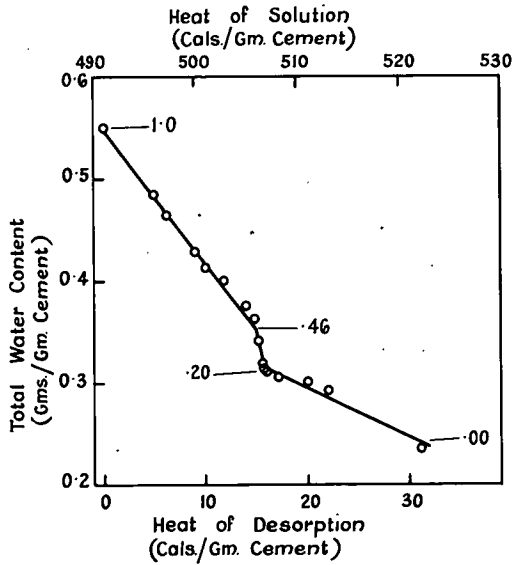


Figure 5. Relationship between heat of desorption and total water content at designated relative vapor pressures.

TABLE 1  
POINTS OF INFLECTION AS A FUNCTION OF VAPOR PRESSURE

Item	Relationship	Relative Vapor Pressure at Point				
		B	C	D	E	
First desorption, Bar 1	$p/p_o$ vs $\Delta L$	0.75	0.49	0.34	0.15	
	$p/p_o$ vs $\Delta W$	0.74	0.48	0.34	0.16	
	$\Delta W$ vs $\Delta L$	0.74	0.47	0.34	—	
First desorption, Bar 2	$p/p_o$ vs $\Delta L$	0.70	0.45	0.33	0.18	
	$p/p_o$ vs $\Delta W$	0.70	0.43	0.33	0.18	
	$\Delta W$ vs $\Delta L$	0.70	0.43	0.29	0.18	
First adsorption, Bar 2	$p/p_o$ vs $\Delta L$	K	J	I	H	G
	$p/p_o$ vs $\Delta W$	0.97	0.85	0.67	—	0.31
	$\Delta W$ vs $\Delta L$	0.97	—	0.70	—	0.37
Second desorption, Bar 2	$p/p_o$ vs $\Delta L$	M		N		
	$p/p_o$ vs $\Delta W$	—		0.36		
	$\Delta W$ vs $\Delta L$	0.63		0.36		
		0.68		0.36		

Figure 4 that breaks occur in the curve at points representing  $p/p_o$  values of 0.44 and 0.20, but that shrinkage is a linear function of the heat of desorption for  $0 < p/p_o < 0.20$  as well as for  $0.90 > p/p_o > 0.44$ . A less expected result is that the slopes of these two segments of the curve appear to be parallel. This suggests that there is a constant relationship between the shrinkage and the heat of desorption except for  $0.44 > p/p_o > 0.20$  and  $p/p_o > 0.90$ . It should further be noted that the point representing saturated

vapor pressure conditions lies on the line through the points for  $0 < p/p_o < 0.20$ . Results on other cements are required to confirm this finding before an explanation of its significance is made. For  $0.44 > p/p_o > 0.20$  the relationship between the shrinkage and the heat of desorption is significantly different from those for  $0 < p/p_o < 0.20$  and  $0.90 > p/p_o > 0.44$ .

In Figure 5 the relationship between the total water content of the paste when tested and the heat of desorption may be represented by three straight lines. Once again for  $0.46 > p/p_o > 0.20$  there is a break in the curve, but in contrast to the results in Figure 4 the slopes of the other two portions are not parallel. The removal of a certain amount of water at low  $p/p_o$  values leads to a greater change in the heat of desorption than a similar change at higher relative vapor pressures.

The values of the relative vapor pressure at which breaks occur in Figures 4 and 5 are close to those observed in the shrinkage/weight-loss curves already described.

#### Shrinkage/Weight-Loss Relationship Using Sorption Balance and Extensometer

In Figures 6 to 11 the results of the changes in weight and length of the bars are presented. It is obvious that the curves are not of the type usually observed but consist of stepped portions, suggesting that at specific vapor pressures some phenomena occur which affect both the length and weight of the specimens. It should be borne in mind when considering the figures that at point A the water in the macropores has already been removed, and the weight loss represents removal of water from capillaries and cement gel only. The points of inflection as a function of the vapor pressure are given in Table 1, where  $p/p_o$  represents the relative vapor pressure,  $\Delta L$  the change in length and  $\Delta W$  the change in weight of the specimen.

The first obvious break in the curves occurs at point B, which corresponds to a relative vapor pressure of between 0.63 and 0.75 with an average close to 0.70  $p/p_o$ . Two possible explanations of the break at B can be proposed. The first is that a specific hydrate undergoes dehydration at this point; the second is that water in larger pores is being emptied through pores of smaller capillary radius. It appears that this break is common to both desorption and adsorption cycles since changes in slope occur at points I and M, which are close to 0.70  $p/p_o$ .

Powers (11) suggests that at relative vapor pressures below about 0.45, phenomena arising from molecular cohesion of water disappear since the hydrostatic tension exceeds the fracture strength of water at this stage. Therefore it is interesting that the next break in the curves is at point C, which is close to  $p/p_o = 0.45$ . This point is taken to indicate the commencement of the breakdown of menisci within the capillaries of the paste. It is considered, however, that this phenomenon exercises its maximum effect at point D where a large weight change is accompanied by small shrinkage in the case of bar 2, and indeed a slight expansion in the case of bar 1. Between points C and D, however, a general decrease in the shrinkage/weight-loss ratio is noted. The water removed up to point C, i. e.,  $p/p_o = 0.45$ , is once again considered to be held by capillary condensation. It does not appear as if the break at point C has a counterpart in the first adsorption curve although a possible break exists at point H which corresponds to  $p/p_o = 0.48$ . On the other hand, the break at point D has counterparts in point G and N in the first adsorption and second desorption cycles.

Point E is at  $p/p_o = 0.17$  and, although not obvious from the curves presented, since they end at  $p/p_o = 0.05$ , it heralds the onset of increasing shrinkage/weight-loss ratio, which continues to a stage where heating is required to remove the most strongly bound water in the paste.

As mentioned, the first adsorption curve changes slope at about  $p/p_o = 0.33$  and 0.68, which correspond to B and D on the desorption curve. The adsorption curves show an important change in slope at point K which appears to be due to condensation in capillaries outside the cement gel per se. As indicated by Powers and Brownyard (10) this distinction between capillary water and gel water is arbitrary since the mechanism of adsorption may be the same but the concept is helpful for the interpretation of the changes in slope of the curve.

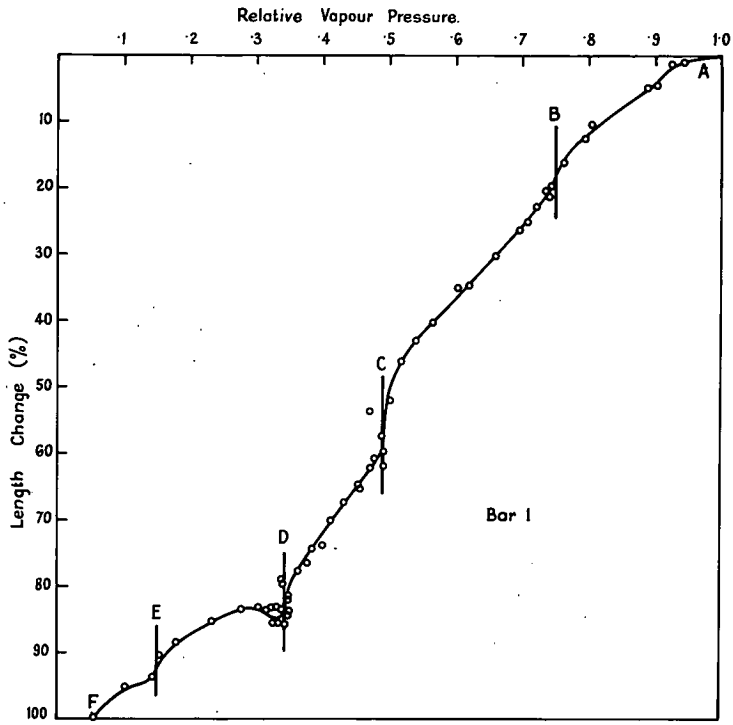


Figure 6. Relationship between relative vapor pressure and length change.

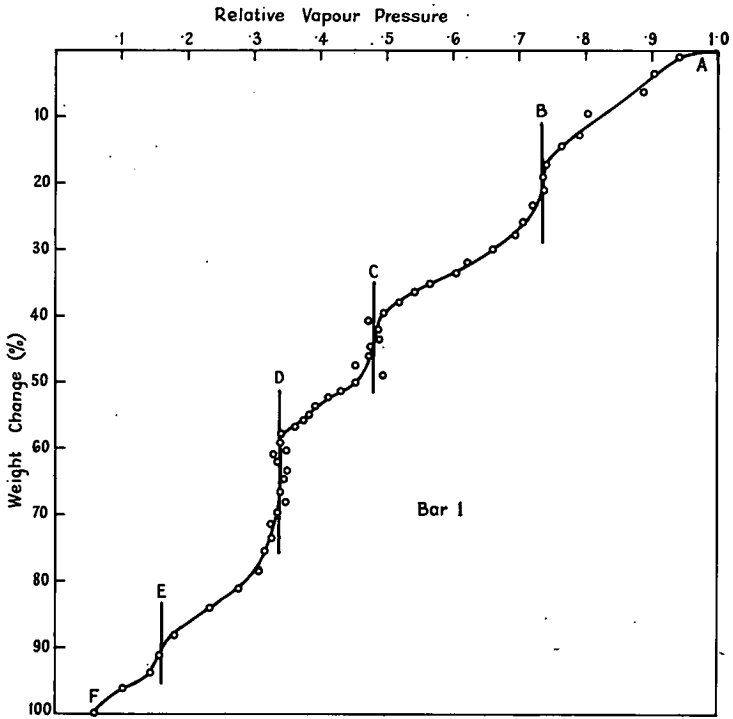


Figure 7. Relationship between relative vapor pressure and weight change.

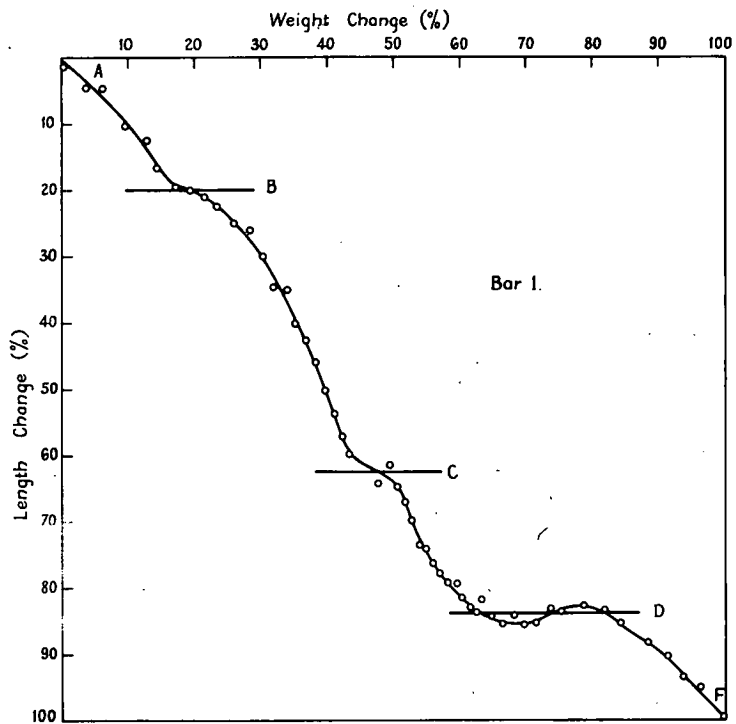


Figure 8. Relationship between weight change and length change.

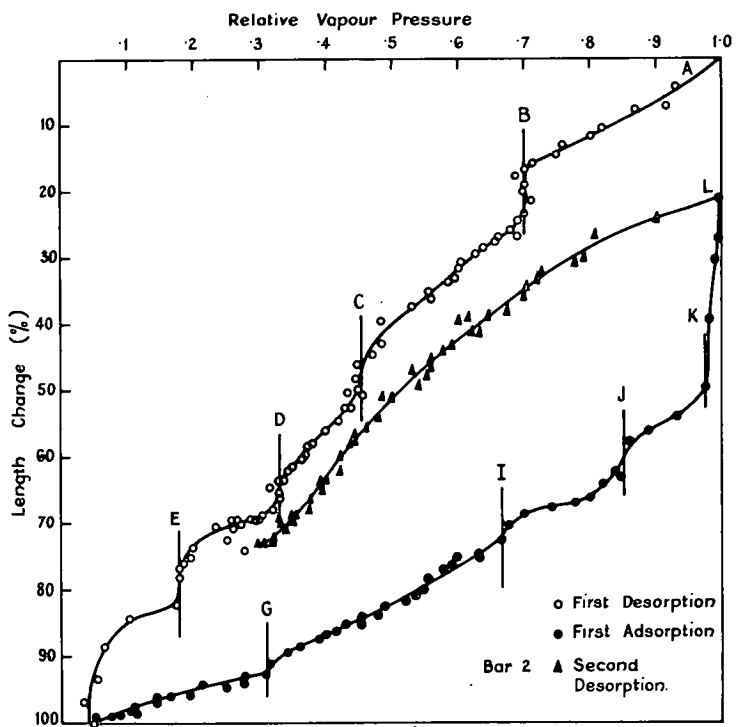


Figure 9. Relationship between relative vapor pressure and length change.



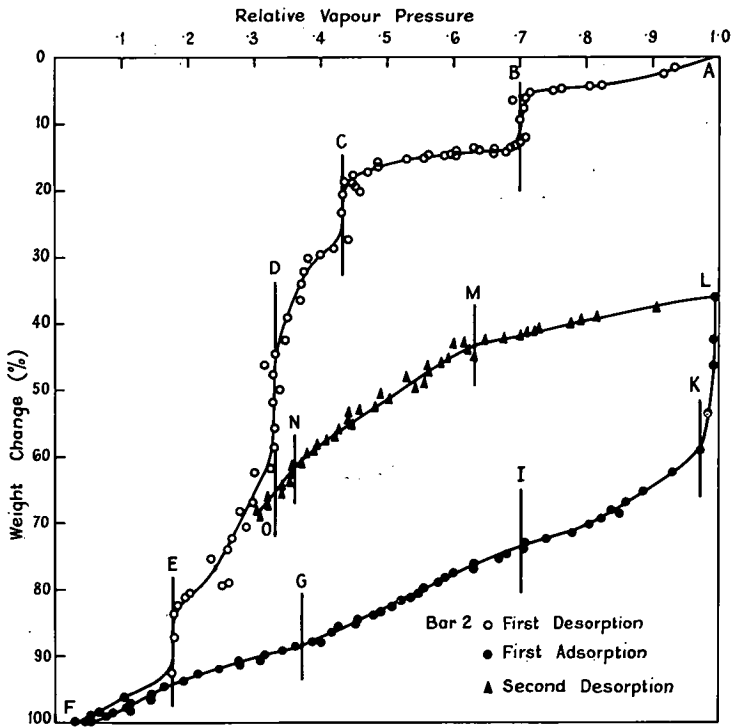


Figure 10. Relationship between relative vapor pressure and weight change.

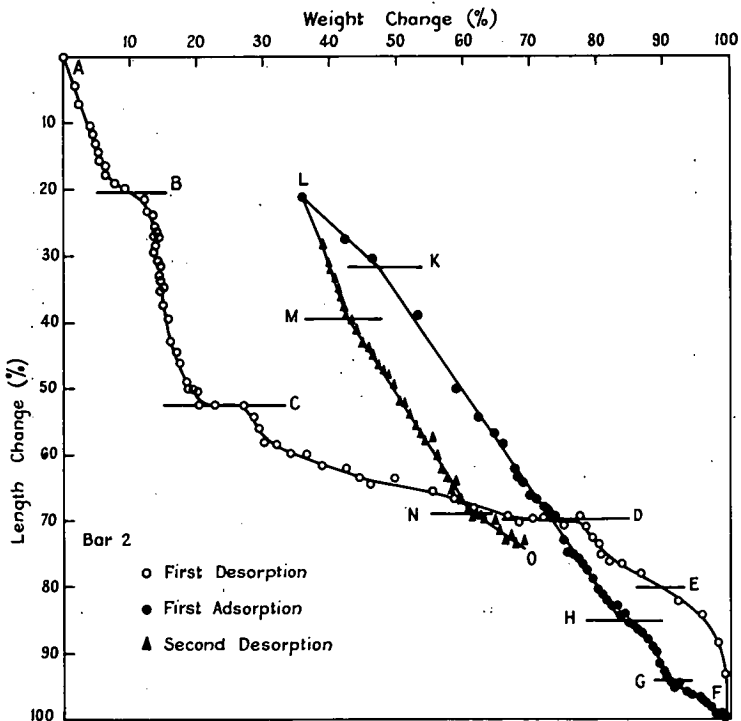


Figure 11. Relationship between weight change and length change.

The breaks at points J and H are less obvious than those mentioned above, and, whereas H may correspond to C in the desorption curves, J appears to be unrelated to any other break.

In the second desorption curves breaks exist at M and N, which again indicates that the phenomena observed at these two points are reversible and can be observed during cyclic drying and wetting. A further point to be noted in all of the curves of bar 2 is the hysteresis, which is less pronounced between the first adsorption and second desorption cycles than between either of these and the first desorption cycle.

One question remains: What similarities do the curves obtained by means of the sorption balance bear to those obtained by more conventional measuring techniques? If Figures 2, 8 and 11 are compared, it is observed that the curve given in Figure 8 and the first desorption curve on Figure 11 may be closely approximated by a series of straight lines as in the case of Figure 2, provided that small changes, particularly at points B, are ignored. All three curves show the common features of a steep slope followed by a section where a large loss in weight is accompanied by little shrinkage. This section in turn is again followed by a steep slope. The relatively small breaks at B, C and E would not be observed by conventional measurements. Fortunately, they do not affect the general relationship between shrinkage and weight change, although they do indicate the precise points at which changes occur. If their existence is proved for cement pastes in general, then certain theories about the continuous loss of water from the paste may require revision.

#### GENERAL CONCLUSIONS

From the foregoing results it appears to be possible to differentiate between various types of water lost from a cement paste. Not only is this information important from a basic research viewpoint but the relationships between these types of water loss and the accompanying shrinkage are important in any endeavor to reduce shrinkage in concrete.

It is logical to conclude, in a way similar to Kalousek (12) and Powers (11), that at high relative vapor pressures shrinkage is caused largely by capillary-tension stress. At lower relative vapor pressures these stresses cease to exist, and the change in forces may lead to slight expansions of the sort observed in the case of bar 1 (Fig. 8). As suggested by Kalousek (12), desorption of interlayer water at this stage may either balance the expansion or cause further shrinkage. Ultimately, however, the removal of the last amounts of evaporable water causes substantial shrinkage of the paste. It therefore follows that any method which reduces the capillary-tension stress in concrete should reduce shrinkage. Only further knowledge of the capillary structure of cement pastes will permit the computation of these forces and possible solutions to shrinkage problems.

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