out that the slump in the case of the standard portland was 2-in. less than for the air-entraining or blended cements.

2. The amount of shrinkage or swell in all cases is not of such magnitude as to seriously affect the finishing operations or the smoothness of the finished pavement.

3. The delay in finishing operations up to the point where finishing can be properly done does not reduce the resistance of the concrete to freezing and thawing.

4. More uniform concrete, as measured by resistance to freezing and thawing, and as indicated by the difference in resistance of the top and center discs is obtained with the use of cements or cement blends which result in the entrainment of air in the amounts found in this study.

5. In view of the fact that the same load was used in all cases for the determination of the end point the data does not accurately measure the relative resistance to freezing and thawing of the different cements used in the study.

1947 Field Results—While the final finishing operations on the 1947 jobs were not delayed as much as this study would indicate to be possible, they were carried on, in general, somewhat later than was the case in 1946. The riding qualities of the 1947 jobs are generally much better than the 1946 jobs. It may be significant that on the best 1947 job, the longitudinal power-floating and the straightedge finishing were both carried on later than on the other jobs.

A DISCUSSION OF CEMENT HYDRATION IN RELATION TO THE CURING OF CONCRETE

T. C. Powers, *Manager of Basic Research, Portland Cement Association*

SYNOPSIS

The question of the amount of water required to hydrate cement is somewhat irrelevant to the question of proper curing. Cement hydration is discussed to show why this is so. The minimum amount of water required to bring cement to its ultimate degree of hydration (which may not be complete hydration) is, for an average cement, about 0.44 gram of water per gram of cement, plus the curing water that must be added to keep the paste saturated. This amount of water is the minimum that will provide space for the hydration products.

Curing procedures should be such as to keep the concrete as nearly saturated as possible until the originally water-filled space has become filled with hydration products to the desired minimum extent. For maximum hydration concrete must be kept saturated or nearly so because hydration products can form only in water-filled space and only in that part of the water-filled space that is outside the gel-substance, that is, only in the water-filled capillaries in the paste. Concrete sealed against evaporation must initially contain more than about 0.5 g. of water per g. of cement to assure full hydration, since self-desiccation progressively reduces the space available for hydration products. Even if full hydration may ultimately be reached, self-desiccation greatly reduces the rate of hydration.

Samples stored in water vapor (or in water vapor and air) in which the vapor pressure is about 80 percent of the saturation pressure, or less, will practically cease hydrating when the water evaporable at this pressure is lost, apparently because the capillaries become emptied at that pressure.

Procedures required to produce maximum cement hydration, namely, those that would produce and maintain the maximum degree of saturation, would not generally be justified. Self-desiccation, and even some loss by evaporation, is beneficial in some respects. Membrane curing will not assure full hydration but may be adequate and desirable, especially for concrete members in contact with soil.

Curing as applied to concrete may be defined as a procedure for promoting hydration of portland cement. It generally implies control of moisture loss and sometimes of temperature. A full discussion of this topic would lead to various ramifications such as curing at steam pressures above one atmosphere, intermittent application of curing water, effect of temperature variations during the early stages, etc. This discussion will be confined to some features of the chemistry and physics of cement hydration in relation to curing. It deals with the factors that control the rate and extent of cement hydration. The various ways in which curing influences the useful properties of concrete are conside ed to a limited extent only.

It might be supposed that once the danger of initial surface-crazing is passed the concrete needs to retain only the amount of water that will meet the chemical requirements of the cement. That is, it would seem that we need only to ascertain the minimum amount of water required for adequate hydration and then to specify a procedure that will ensure the retention of this amount for the required length of time. However, experimental study shows that to meet the minimum requirements of such specifications would not produce the result expected.

The amount of water that is required to meet the chemical requirements of the cement cannot be stated in terms of simple, chemical formulae. However, for the present purpose it is sufficiently accurate to say that an average cement can combine with an amount of water equal to about one fourth of its own weight. But if only this amount of water is retained by the concrete during the period of curing, not more than half of the retaine 1 water will ever react with the cement, no matter how long the water is retained by the concrete. Moreover, it makes no difference how great the excess of cement may be. Lasseter (*1*)[1] studied samples containing as much as 17 g. of cement per g. of water and found that even after months of curing about half the water remained free to evaporate and most of the cement remained unhydrated. Likewise, in this laboratory (*2*) specimens containing 8 g. of cement per g. of water were found to contain both free water

and unhydrated cement after four years of curing under water at 70 to 75 F.

The ability of cement to remain unreacted in the presence of free water can be explained as follows: Consider a quantity of cement grains totaling 1 cu. cm., absolute volume. Experiments show that the grains making up this volume must be distributed through at least 1.4 cu. cm. of water in order for all the cement to become hydrated.[2] The reason for this is that 2.4 cu. cm. is the least volume that 1 cu. cm. of cement can occupy after it has become hydrated. In other words, the hydration products require the space occupied by the original cement and additional space equal to 1.4 times the volume of the cement. Thus we see that not less than 1.4 cu. cm. of water-filled space per cu. cm. of cement is required in the fresh paste simply to provide the room required by the amount of hydration products that can be derived from 1 cu. cm. of cement. A simple calculation will show that this amount of water per unit volume of cement corresponds to about 0.44 g. of water per g. of cement, or, inversely, 2.25 g. of cement per g. of water. This explains why in samples containing as much as 17 g. of cement per g. of water most of the cement remains unhydrated —the amount of water-filled space in the paste can accommodate only a small fraction of the possible amount of hydration products.

The continued presence of uncombined water in hardened cement pastes containing an excess of cement is due to the existence of very small pores in the cement gel, which is the major constituent of the hydration products. Experimental data indicate that the gel pores can hold an amount of water about equal to the amount that is combined with the cement.

For reasons that will be given further on, any residues of unreacted cement in the paste cannot react with the free water unless there is enough free water present to more than fill the gel-pores. At any given time, the amount of water present in the concrete must be greater

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[1] Italicized figures in parenthesis refer to list of references at the end of the paper.

[2] More accurately we should say, "in order for the maximum possible fraction of the cement to become hydrated since some of the cement may remain unhydrated, however long the curing period." For simplicity such a qualification will be omitted at this stage of the discussion.

than twice the amount that has become combined with the cement up to that time, else hydration will cease. As will be seen from later parts of this discussion, the necessity for a certain minimum amount of water-filled space to be present throughout the period of curing may require the addition of curing water to compensate for the "self-desiccation" that is produced by the process of hydration. For this reason sealing concrete against gain or loss of water may not assure complete hydration.

Even if a sufficiently high degree of saturation is maintained indefinitely, some of the cement may remain unhydrated; that is, the maximum possible hydration may not be complete hydration. From the observation of Brownmiller (*3*) and from data obtained in this laboratory, it appears that the final unhydrated residue is proportional to the coarse fraction of the original cement, that is, the fraction retained on, say, the 200-mesh sieve; most if not all the material passing that sieve will in time become completely hydrated if the water-filled space is ample. The rate of hydration of the coarser particles apparently becomes negligibly low after the particles become surrounded with a thick layer of gel.

Up to this point we have discussed the conditions that must be maintained to hydrate the maximum possible fraction of the original cement. It should not be concluded, however, that such is the proper objective of curing. The fact is that for developing the potential qualities of concrete, thorough curing does not necessarily require complete hydration of the cement. If strength, for example, depended primarily upon the extent of cement hydration, it would be necessary to avoid the use of cement pastes that contain less than 0.44 g. of water per g. of cement, since, as we have seen, some of the cement must remain unhydrated if any smaller amount of water is used in the fresh paste. But experiments show that strength at any given age continues to increase as the water content is reduced below 0.44 per g. of water per g. of cement, provided that a state of saturation or near saturation of the paste is maintained. The strongest materials yet made with portland cement were neat cement cylinders, molded under pressure, the cylinders containing about 0.08 g. of water per g. of

cement. Very little of the cement in these cylinders could have become hydrated.[3]

Even though the qualities of concrete may not be closely related to the degree to which the cement is hydrated, they do depend very largely on the degree to which the original water-filled space in the fresh paste becomes filled with hydration products. For example, if 80 percent of the originally available space in each of two different pastes made with the same cement becomes filled with hydration products, the strengths of the two pastes will be equal even though in one case 75 percent of the cement may be hydrated and in the other, 95 percent (*5*). However, since the pastes in most concretes contain more water-filled space than can be filled with hydration products, qualities such as strength and impermeability are generally better the closer the approach to the maximum possible degree of hydration.

As already pointed out some of the cement may remain unhydrated even when there is ample water-filled space in the paste. Under such circumstances the persistence of an unhydrated residue could be prevented by grinding the original cement finer. However, there is no clear indication that the quality of present day concrete could be improved by so doing. As a matter of fact, there is evidence that the presence of unhydrated cement in concrete may be beneficial, though the reasons for the benefits are not clearly seen.

Thus we see that curing procedures need not be aimed toward obtaining complete combination of either the cement or the water; the first may not be necessary or desirable, and the second is impossible. Rather, curing procedures should be such as to keep the concrete as nearly saturated as possible until the original water-filled space has been filled with hydration products to the desired minimum extent.

What has been said above is the gist of our practical knowledge of cement chemistry and physics in relation to the question of curing under ordinary circumstances. In the rest of this paper we shall present supporting evi-

[3] According to a private communication from M. A. Swayze, this material was prepared under the direction of Duff A. Abrams in the laboratory of the Lone Star Cement Corp. Strengths as high as 40,000 lb. per sq. in. were obtained. This is equal to the strength of natural stones such as granite, dolomite, or basalt.

dence and point out some perhaps less obvious implications of the views already given.

FACTORS INFLUENCING THE RATE AND AMOUNT OF CEMENT HYDRATION

For a satisfactory consideration of this question it is necessary to recall some of the facts about the colloid and capillary characteristics of hardened concrete.

If saturated concrete is placed in saturated air, it will not lose weight, but if it is placed in air in which the vapor pressure is even slightly below that of saturated air, the concrete will lose water by evaporation. When water is lost by evaporation, it is believed to come from two classes of spaces within the hardened paste, the gel pores and the capillary pores.[4] When the degree of saturation is relatively high, increases or decreases in water content affect mainly the capillary pores.

When the vapor pressure of the atmosphere changes, the moisture content of the concrete changes also; it rises with rise in humidity, and vice versa. Variations in moisture content of concrete that result from variations in humidity are due to the effects of dissolved salts, capillary tension and adsorption forces, mainly the last two. These factors reduce the tendency of the water in concrete to evaporate, relative to the normal tendency of pure water. The reduced tendency to evaporate is spoken of as a reduced vapor pressure. The magnitude of this effect increases as the degree of saturation is reduced and vice versa. Hence, a given sample of concrete when stored in water vapor at fixed pressure will finally, by gain or loss of moisture, reach a state such that the vapor pressure of the water retained in the concrete is the same as that of the vapor in the surrounding space. Thus it is that the degree of saturation of concrete exposed to air depends upon the degree of saturation of the surrounding atmosphere.

The degree of saturation of the surrounding atmosphere may best be expressed in terms of relative vapor pressure. For example, when the partial pressure of the water vapor in the atmosphere is one-half of what it is when the atmosphere is saturated at the same temperature, the relative vapor pressure is one-half.

[4] Some may come also from the aggregate, but that need not be considered here.

This corresponds, of course, to a relative humidity of 50 percent.

Among those experienced with concrete testing it is common knowledge that soon after test-specimens are stored in room air the cement apparently ceases to hydrate. This is shown by the lack of strength-gain except for that due to drying itself (6). The question is how does partial drying influence the rate of cement hydration and how dry may the concrete become without stopping hydration altogether? This question involves not only concrete partially dried by evaporation but also concrete that has been sealed against evaporation, for sealed concrete will also become partially dry through self-desiccation (7), giving rise to what Harmer E. Davis (8) and M. A. Swayze (9) have called autogenous shrinkage.

Experimental Observations—Leopold Jesser (10) stated that portland cement stops hydrating when the concrete dries to the point where the relative water vapor pressure of the residual water falls below 80 to 90 percent of the saturation pressure. V. Rodt (11) reported that the rate of hydration is very slight but measurable when the relative vapor pressure is 0.5 p_s (p_s = water vapor pressure in saturated atmosphere), and that the rate increases as the relative vapor pressure is increased.

Data published by Gause and Tucker (12) are especially interesting. These authors placed fresh cement pastes in bottles, sealed the bottles, and from time to time measured the vapor pressure inside the bottles. Their results are plotted in Figure 1, which shows how the pressure changed during the first four or five weeks of hydration.

Note that in most cases the pressure dropped at a progressively diminishing rate, the rate becoming small after the first two weeks, with one exception. The exception is the paste of the highest water ratio (w/c = 0.32) made with Type II cement. The pressure over that paste did not begin to decrease until after the 15th day. It is surmised that the first two weeks were required to absorb the water accumulated on top of the sample during the period of bleeding. The other samples must have been too stiff to bleed appreciably.

It will be shown that the lowering of the vapor p essure is due to self-desiccation, which is proportional to the extent of hydration. Hence, cessation of pressure-drop indicates cessation of hydration.

Considered by themselves, these data do not indicate complete cessation of hydration within the period of observation; in all cases the last observation indicated a slightly lower pressure than the previous one. However, in connection with other observations they may be taken to indicate that in a sealed container the hydration of the cement will not cause the vapor p.essure to drop much below 0.75 p_s or

percent relative vapor pressure remained free-running and did not change in appearance. At 70 percent relative vapor pressure the sample became somewhat lumpy; at 80 percent it formed a caked mass which, however, could be b:oken up without much difficulty; at 89 percent the mass was harder; in a saturated atmosphere the sample became a solid cake of such strength that it could not be broken up without destroying the glass container.

These experiments and observations indicate that the vapor pressure must be maintained at a comparatively high value if useful hydration is to proceed at an appreciable rate.
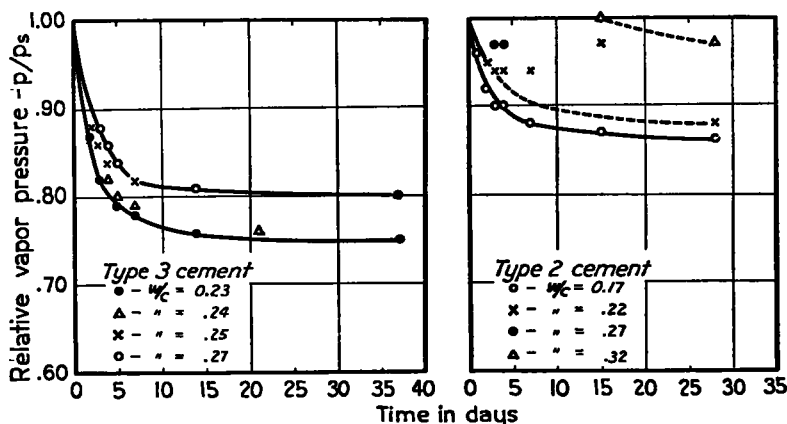

Figure 1. Reduction of Vapor Pressure over Sealed Pastes—Data from Gause & Tucker

$0.80 \ p_s$. Other features of these data will be discussed further on.

In an experiment made in this laboratory portions of unhydrated commercial Type I cement were stored in atmospheres of various controlled vapor pressures. Samples of each portion were taken from time to time, and the amounts of water taken up, both total and non-evaporable, were determined. The results after 6 months exposure are given in Figure 2. Note that the average rates of hydration during a 6-month period (as indicated by the total amount of water taken up by the cement) was comparatively low for vapor pressures below 0.8 of the saturation pressure. Below $p = 0.3 \ p_s$ the rate is negligible. These results in general are in agreement with the observations of Jesser and Rodt mentioned above.

In our experiments all samples of cement stored in atmospheres having less than 50

Interpretation of Experimental Results—Until more is known about the chemistry and physics of cement hydration, interpretation of the results cited above must be given and should be received with some mental reservation. However, the physical factors discussed below must play a very important if not controlling role.

We note first that hydration can proceed until the cement reaches its maximum[5] degree of hydration or until the available space is filled by hydration products, whichever limit is reached first. Next we observe that the space available for hydration products, particularly the cement gel, is the water-filled space only. This is shown most obviously by

[5] As mentioned before, for a very finely ground cement the maximum degree may be complete hydration, but for ordinary cements the maximum is less, since residues of the coarsest grains remain unhydrated.

the inability of the hydration products to fill cavities such as air bubbles in the paste.

The fact that the cement gel can be laid down only in water-filled space is particularly significant with respect to the results shown in Figure 2, for those results seem to be ex-
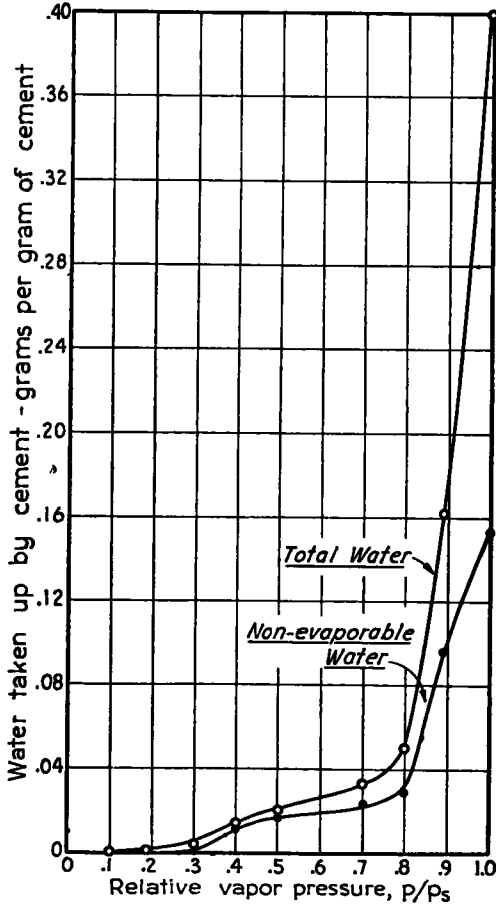
Figure 2. Amounts of Water Taken Up by Dry Cement Exposed to Water Vapor for Six Months.

plainable in terms of the amount of liquid water with which the cement is in contact under given atmospheric conditions. When dry cement is exposed to water vapor, capillary condensation will occur within the bed of dry particles (13). Condensation should occur at points of contact between the grains. The principle involved is illustrated in Figure 3. The condensed water is shown in the form of a ring that has collected around a point of contact between two spheres.

As shown in Figure 3, a ring of condensed water will present two principal curvatures, one being concave toward the exterior and the other convex. When equilibrium between the condensed water and the existing vapor pressure has been established, the curvatures
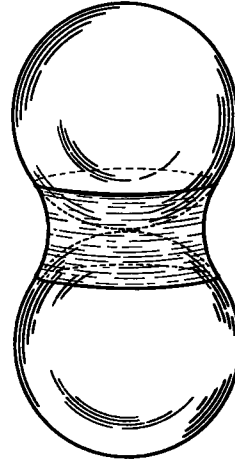
Figure 3. Diagram of a Ring of Water around the Point of Contact between Two Spheres

at any point on the exposed water surface must be such as to satisfy the Kelvin equation:

$$\frac{1}{r_1} + \frac{1}{r_2} = -\frac{RT}{M v_f \sigma} \ln \frac{p}{p_s},$$

where r_1 = radius of concavity,
r_2 = radius of convexity,
σ = surface tension of the water,
v_f = specific volume of water
M = molecular weight of water,
R = gas constant,
T = absolute temperature,
ln = natural logarithm,
p = existing vapor pressure, and
p_s = pressure of saturated vapor.

The shape of the water-ring is determined by the conditions that; (1) the water surface is tangent to the solid surface at the margin of the ring; and (2) the curvature of surface at any point must satisfy the Kelvin equation. This means that the volume of liquid in the ring must vary with the relative vapor pressure, p/p_s.

From the geometry of the ring, it is apparent that the two radii of curvature must have opposite signs; hence, equilibrium with a given vapor pressure is established when the difference between the two radii of curvature is such as to satisfy the above equation. The equation shows that when the existing vapor pressure is equal to the saturation pressure p_s, the two radii must be equal. When this equality is established, the volume of the ring is at its maximum. At equilibrium with the saturation pressure, the radius of concavity will be equal to the radius of the sphere.

From the relationships just reviewed the corresponding relationships for systems composed of non-spherical particles can be comprehended. It can be seen that the lower the relative vapor pressure the smaller will be the volume of the water ring, and that the interparticle spaces cannot become completely filled by capillary condensation, even at the saturation pressure.

The various degrees of hardness developed by the different samples of dry cement in the experiment described above can now be accounted for. Since the hydration products can be laid down only in water-filled space, the amount of hydration that can take place in a bed of dry cement particles exposed to water vapor must be limited by the volume of the condensed water which in turn is controlled by the vapor pressure. The grains became cemented together by gel laid down in the rings of water at the contact-points in the bed. The higher the vapor pressure the larger the ring and hence the larger and stronger the connecting links of hydration products.

These observations on the hydration of cement exposed to water vapor show also how partial drying limits cement hydration in concrete. Wherever the paste in concrete is not water-saturated, the residual water must exist as adsorbed layers on the internal surfaces of the hardened paste and, if the water content is not too low, as small bodies of capillary-condensed liquid such as rings around points of contact, or segments of liquid in cavities. Since the hydrates can deposit only in the water-filled spaces, the amount of hydration must always be restricted by partial drying. The rate of hydration will also be affected since capillary condensed water can cover only a fraction of the boundary area of the solid phase. Even in those regions where the

water rings exist, the reaction rates may be relatively low owing to a lowered chemical activity coefficient of the water. The lowering of the activity coefficient is indicated by the lowering of the vapor pressure of the water. It influences reactions in about the same way as a reduction in ion-concentration.

The effects just described have been verified at least qualitatively in various experiments. We have already pointed out the observations of Jesser, Rodt, and Gause and Tucker. In this laboratory many experiments have been made with granules of hardened paste that were first dried and then exposed to water vapor at various pressures. All the samples at first gained rapidly in weight by adsorption and capillary condensation. Those exposed to pressures of about 0.8 p_s and higher then continued to gain in weight very slowly over a long period, whereas those exposed to the lower pressures showed no gain following that due to adsorption.

From the information just reviewed it appears that we are justified in arriving at a tentative answer, at least, to the question raised at the beginning of this section; How does partial drying influence the rate of cement hydration and how dry may the concrete become without stopping hydration altogether? We may conclude that for practical purposes hydration stops before concrete dries to the degree where the residual water exhibits a relative vapor pressure of about 0.8 p_s and that useful hydration stops at this pressure probably because the capillaries are empty, or practically so, at that and lower pressures. This conclusion must be somewhat qualified, as will be shown farther on.

Self-Desiccation—As mentioned before, the drying of concrete can occur even if loss by evaporation is prevented. This phenomenon, called self-desiccation, will now be considered further.

Suppose that a fresh paste contains w_o grams of water after bleeding. After a given period of curing under water, the water content of the same sample will be a larger quantity, w_t. The increase in water will be called Δw, that is,

$$\Delta w = w_t - w_o \qquad (1)$$

If the specimen containing w_o grams of water had been sealed against gain or loss of

water, it could not have gained in weight by the absorption of water as it did when cured under water. Hence, the hydration of cement in a sealed specimen produces a deficiency in its water content with respect to the amount required for saturation. In other words , for a sealed specimen Δw of equation (1) is the amount of water that would have to be given to a sealed specimen to saturate it.

Since the only space available for hydration products is that part of the capillary space that remains water filled, we may conclude that as hydration proceeds, the water-filled space in a sealed specimen diminishes more rapidly than it does in a water-cured one. When Δw becomes equal to the capillary space in a sealed specimen, that is, when self-desiccation has gone so far as to empty the capillaries, hydration will cease. This condition may be reached while the paste still contains a considerable amount of evaporable, chemically free water in the gel.

The experiments with dry cement described in the preceding section indicate that capillary condensed water should disappear when the vapor pressure drops below about 0.8 p_s. The data of Gause and Tucker (Figure 1) support this conclusion but at the same time indicate that the phenomenon is not quite as simple as has been indicated up to this point. Referring again to Figure 1, we see that self-desiccation lowers the vapor pressure as anticipated. However, with a given cement the curves level off at different pressures, the final pressure being higher the higher the original water-cement ratio. Also, with the same water-cement ratio but with different cements, the curves level off at different pressures. The indicated range of leveling-off pressures is from 0.75 p_s to somewhere below 0.85 p_s.

These data thus indicate that the relative vapor pressure alone may not be an accurate index to the amount of water in the capillaries. It seems probable that the differences in vapor pressure at which hydration ceases are due to differences in the concentration of dissolved electrolytes in the evaporable water, particularly the alkalies. With a given cement the curve representing the lowest water-cement ratio levels off at the lowest pressure because the electrolyte concentration is highest. The same reasoning would lead us to expect that with cements of different alkali contents the leveling off pressures should be different at the same water-cement ratio. The values of p/p_s plotted in Figure 1 correspond to reported relative humidities (as reported by Gause and Tucker), which is the same as reporting relative vapor pressure on the basis of the saturation pressure of pure water. Had it been possible to express p/p_s on the basis of the saturation pressures of the electrolyte solutions, the curves might have leveled off at the same relative vapor pressure.

It thus appears that with the reservations concerning variations due to electrolyte concentrations we are justified in concluding that in hardened paste useful hydration will cease when drying reduces the vapor pressure to about 0.8 p_s, the exact leveling off pressure depending on the characteristics of the cement and on the water-cement ratio. This conclusion applies whether the drying is due to loss by evaporation or by self-desiccation. It appears also that useful hydration ceases at pressures below about 0.8 p_s because appreciable amounts of evaporable water do not exist in the capillaries of the paste at lower pressures.

Water Loss at Which Hydration Ceases—We have seen that reducing the evaporable water content either by evaporation loss or by self-desiccation will stop hydration. The question now arises as to what amount must be lost to bring about this condition.

The answer could be derived most simply from experimental data showing the relationship between the degree of saturation and the rate and amount of hydration for pastes of various compositions. However, such data are not now available. We must answer the question as best we can from data bearing on the question more or less indirectly.

The amount of water that must be lost from a given paste to stop hydration can most easily be estimated from the assumption that at any time hydration can occur only in the water-filled part of the capillary system in the paste. At any given stage of hydration the amount of water-filled capillary space (as distinct from space in the gel—gel pores) can be stated as follows:

water-filled capillary space =
$$w_o - \Delta V_B - \Delta v_u \quad (2)$$
where w_t = total original water-filled space,

ΔV_B = increase in over-all volume (bulk volume) of the solid material inside the boundaries of the paste,

and Δv_w = evaporable water lost by evaporation or self-desiccation.

From the Powers-Brownyard paper we find that, for an average cement,

$$\Delta V_B = 5.5 \, w_n v_c \qquad (3)^6$$

where w_n = non-evaporable water, and
     v_c = specific volume of the original cement.

For an average cement, $v_c = 0.317$. Hence,

$$\Delta V_B = 1.74 \, w_n$$

Also, for self-desiccation, it was shown in the same paper (p. 986) that

$$\Delta v_w = 0.279 \, w_n \qquad (4)$$

For self-desiccation,
available space

$$= w_o - 1.74 \, w_n - 0.279 \, w_n$$
$$= w_o - 2.02 \, w_n \qquad (5)$$

From equation (5) it follows that if the hydration of a sealed specimen has proceeded to the point where the non-evaporable water has become about one-half the original water content, the capillaries will have become empty and hydration will have ceased. It follows also that full hydration of the cement in a sealed specimen cannot occur unless the original water content is at least double the maximum possible value of w_n. For an average cement, maximum w_n/c is about 0.25. Therefore, by equation (5) full hydration of a sealed specimen can occur only if

$$\frac{w_o}{c} = 2.02 \times 0.25 = 0.50.$$

The foregoing estimate cannot be considered exact, even for an average cement, for it is based on the assumption that all the water lost by self-desiccation is lost from the capillaries. Actually, desiccation must affect the gel and the capillaries simultaneously (*14*). However, over the range of loss that concerns us here for pastes having water ratios within

[6] This is obtained as follows: By eq. (10), p. 689, of the Powers-Brownyard paper.

$$V_B = \left(1 + 5.5 \, \frac{w_n}{c}\right) c v_c$$

Then

$$\Delta V_B = V_B - c v_c = 5.5 w_n v_c \,.$$

the practical range (mostly above $w_o/c = 0.55$), the fraction lost from the gel is small and may be neglected.

When evaporation occurs, the loss from a saturated specimen at which hydration stops should be equal to the water-filled capillary space at the time of drying. That is, the drying loss should be

$$w_o - \Delta V_B = w_o - 1.74 \, w_n \qquad (6)$$

Thus the loss at which hydration stops is not a fixed amount, or a fixed percentage of the water required for saturation, but an amount that depends on the extent of hydration and the original water-cement ratio. Incidentally, it may be noted from equation (6) that no water need be lost to stop hydration when (for an average cement) $1.74 \, w_n = w_o$. When this equality obtains, the originally water-filled space is filled with hydration products and hydration can proceed no further whether extra water is available or not.

DISCUSSION OF IMPLICATIONS

Formerly, we have believed that concrete ordinarily contains so much water in excess of that required for hydration that a considerable part of it might be lost without preventing the cement from hydrating normally. It now appears that this view is incorrect. Cement can become fully hydrated only if a sufficiently high degree of saturation is maintained, and it can hydrate at the maximum possible rate (for a given temperature) only if the concrete or paste is fully saturated. It does not follow, however, that good practice requires procedures that will assure the highest rate and degree of cement hydration.

We have observed in the laboratory that if curing water is not supplied during the initial stages of rapid hydration, thus permitting some self-desiccation, subsequent applications of curing water will not restore the maximum possible degree of saturation. Possibly this is due to breaking the continuity of flow in the capillaries. Whatever the reason, the resulting permanent decrease in degree of saturation is believed to increase the ability of the concrete to withstand frost action. Under certain circumstances, this advantage would undoubtedly outweigh the possible slight reduction in cement hydration caused by reduction in water-filled space.

M. A. Swayze (*9*) has pointed out benefits that might result from allowing self-desicca-

tion to occur during the early hours. He showed that self-desiccation can produce shrinkage at the right time to counteract thermal expansion of freshly laid concrete pavement. He says also that it "tends to compact the less dense structure near the top of the slab" during the period of bleeding.[7]

With respect to the use of seal-coats (curing compounds), this discussion can do no more than to point out the effects of applying a perfect or partial seal; it will not deal with the practical limitations or advantages that might be experienced in using commercially available preparations under field conditions. From the information already given it appears that if a perfect seal were applied to fresh concrete, the maximum possible degree of hydration would eventually be reached provided the original water-cement ratio of the concrete was above about 0.5 by weight (However, the time required would probably be far greater than that for water curing). If the seal-coat is not perfectly impermeable, hydration will stop when the total water-loss, including that by self-desiccation, reaches a certain amount depending on the stage of hydration and the original water-cement ratio. For example, consider the following typical data for water-cured pastes made with type I cement:

$\dfrac{w_0}{c}$	Non-evaporable Water at the 14th Day
	g. per g. of cement
0.319	0.152
0.439	0.171
0.537	0.186

On the basis of equation (6) we may compute the water loss (including that by self-desiccation) that would stop hydration in each of these three samples. The results are 14, 33, and 43 percent of w_0/c, respectively. To produce the equivalent of two weeks of water curing a permeable seal-coat would have to hold the losses, including that by self-desicca-

[7] It should be noted that this refers to self-desiccation and not to loss by evaporation. As is well known, early loss of water by evaporation must be prevented to avoid surface cracks. Self-desiccation (which is uniform internal drying) should not by itself produce surface cracks.

tion, below these percentages for a period of at least two weeks.

The data given above show that a test specimen for evaluating commercial curing compounds by some such procedure as that reported by the Blanks, Meissner, and Tuthill (15) should have about the same water-cement ratio as the concrete to be cured in the field. If concrete of a lower water-cement ratio is used in the laboratory test, a given water-loss will reduce the rate of hydration in the test more than would the same loss from the concrete in the field.

All the discussion up to this point has been based on the assumption that the concrete to be cured does not have access to extra water except that which might be furnished in the curing procedure. This condition no doubt exists in the field as, for example, with various types of concrete structural members not in contact with the ground. However, the assumption obviously does not apply to concrete pavement, retaining walls, reservoirs, or any structural member having at least one surface in contact with soil or water. Concrete in direct contact with moist soil receives moisture from the soil continuously and thus maintains a fairly high degree of saturation except perhaps for a region near the surface that is subject to periodic drying.

From Kellermann's summary (16) it appears that several investigators have been discouraged by attempts to study various methods of curing in the field. It seems that differences attributable to differences in curing have not consistently been found. This may be significant, particularly in view of the later tests reported by Long and Kurtz (17) and by Blanks, Meissner, and Tuthill (15). In both these investigations it was found that mere contact with moist soil largely eliminated the influence of variations in curing conditions that were maintained when the specimens were first made. Of course, these findings in no way minimize the necessity of preventing rapid extraction of water from fresh concrete by dry subgrades or by sun and wind; early protection must be provided to prevent crazing and to assure rapid attainment of the specified strength. They merely indicate that the cement in concrete that is in contact with moist soil should eventually become well hydrated without prolonged artificial curing.

All things considered, it seems that even though we may now correct some of our earlier views on cement hydration, we need not materially alter our ideas as to what constitutes good curing practice. If the provisions in standard specifications were followed, structural concrete would remain saturated long enough to develop the specified strength. For uses where the utmost in strength is desirable, as in pavement, present approved procedures plus moisture received from the subgrade should insure adequate curing.

SUMMARY

1. An average portland cement requires about 1.4 cc. of water-filled space per cc. of cement (absolute volume), since about 2.4 cc. is the least volume that 1 cc. of cement can occupy after it has become hydrated. This amount of water, 1.4 cc., is about twice the amount that can become chemically combined.

2. For hydration to proceed, the amount of water present in the concrete at any given time must be greater than twice the amount that has become combined with the cement up to that time.

3. When concrete becomes dried to such an extent that the vapor pressure of the residual water has become about 0.8 normal pressure, cement hydration virtually ceases. The reduction in vapor pressure mentioned is reached when the capillaries in the paste (spaces outside the gel) have become emptied or nearly so.

4. To obtain the maximum possible rate of hydration (at constant temperature), concrete must be kept saturated, or nearly so.

5. Qualities such as strength and impermeability do not necessarily depend on maximum cement hydration. They do depend on the degree to which the hydration products fill the original water-filled space in the paste.

6. Curing procedures need not be aimed toward obtaining complete combination of either the cement or the water; the first may not be necessary or desirable, and the second is impossible.

7. Concrete sealed against evaporation must initially contain more than about 0.5 g. of water per g. of cement to assure maximum cement hydration because of the effect of self-desiccation. Even if maximum hydration may ultimately be reached, self-desiccation may greatly reduce the rate of hydration.

8. Procedures required to produce maximum cement hydration, namely, those that would produce and maintain the maximum degree of saturation, would not generally be justified. Self-desiccation and even some loss by evaporation is beneficial in some respects. Sealing the concrete will not assure maximum cement hydration, but if effectively done may be adequate, especially for concrete members in contact with soil.

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