THE AIR REQUIREMENT OF FROST-RESISTANT CONCRETE

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SYNOPSIS

According to the hydraulic-pressure hypothesis of frost action on concrete the effectiveness of entrained air depends on void spacing. The theoretical maximum permissible spacing is found analytically to be a function of paste properties, degree of saturation of the paste, and rate of cooling. Applied to experimental data from six different pastes, cooled at 20 F. per hour, the theoretical calculations gave spacing factors ranging from 0 01 to 0 026 in. or more, depending on paste characteristics and void size.

A spacing factor for the voids in hardened concrete, as well as the total volume of air, can be calculated from data obtainable by the linear-traverse method The necessary mathematical relationships are given in this paper The actual maximum spacing factor for certain frost-resistant concretes was estimated to be about 0.01 in , a result considered to be in excellent agreement with that obtained from the theoretical calculations. The air requirement is that amount that meets the spacing requirements. In general the air requirement for a given rate of cooling depends upon the paste content, the specific surface of the voids, and the maximum permissible spacing factor.

When voids are too widely spaced to prevent failure of saturated paste, failure will also occur at moisture contents below saturation; within limits, the denser the paste the lower the degree of saturation at failure.

This discussion deals with the problem of predicting the quantity of entrained air required to protect water-soaked concrete from frost damage. In the course of this discussion a revised version of certain phases of the hypothesis on the mechanism of frost action presented four years ago will be developed (*1*).[1] Constructive criticism of the hypothesis as stated previously, and data recently obtained will be taken into account in this revised version

The problem is to estimate the order of magnitude of the hydraulic pressure generated during the process of freezing and to identify the factors that control the magnitude of that pressure. Any such estimate arrived at analytically is bound to be only an approximation; the real conditions are too complex to be represented exactly by workable mathematical relationships. It is possible, however, to arrive at a useful statement of the controlling factors and the relationships between them.

PART 1 THEORETICAL PERMISSIBLE SPACING

Microscopic examination of concrete containing the amount of entrained air required to produce high resistance to the freezing and thawing test reveals that the bubbles are very close together in the paste. It will be shown that the average distance, void to void, through the paste should not exceed 0.02 in., or thereabouts. This means that the maximum distance from a point in the paste to the nearest void is about 0.01 in. or less. The specific surface of average bubbles is about 600 sq. in. per cu. in. If the bubbles were all of the same size, their diameter would be 0.01 in. Thus the spacing of the bubbles is of the same order as their diameters. With these dimensions in mind, we may regard each bubble as being at the center of a small body of paste without seeming too far removed from fact. When freezing occurs, each bubble receives the water expelled from its envelope of paste. Because the regions interjacent to the bubbles are so small, the freezing of a given region and contiguous regions, involving over-all distances of about 0 03 in , can be considered to occur simultaneously. In other words, temperature differences within a given small region can be ignored. It is thus apparent that the hydraulic pressure cannot in general be built up over distances greater than the half-distance between bubbles.

Figure 1 represents a cross-section through

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

a single bubble and that part of the paste within its "sphere of influence" The paste surrounding the bubble contains capillary pores more or less filled with a solution of electrolytes called the freezable water. When the temperature drops below the final melting point,[2] a small fraction of the freezable water will freeze. The lower the temperature, the greater the fraction that will freeze, within the limits to be given in Part 3

The drop in temperature may cause some of the water in the paste to freeze and in so doing to displace some unfrozen water. If the

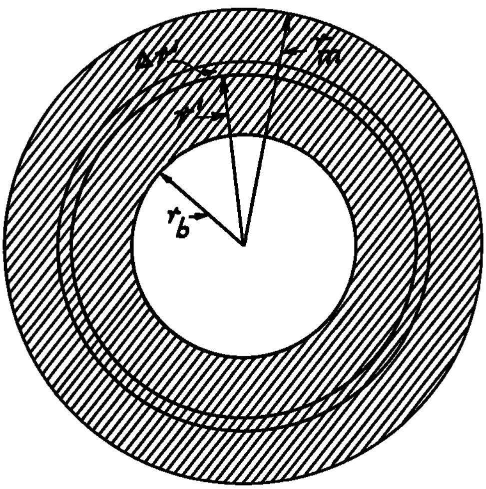

Figure 1. Cross-Section through Air Bubble and Its "Sphere of Influence"

body of paste surrounding a bubble is saturated, the displaced water must either be expelled from the body or the body must expand to accommodate it. If the body expands enough to accommodate the expansion of the water, it is liable to be ruptured, for the required expansion usually exceeds the extensibility of the paste If the water is expelled, the body may not be ruptured, for the pressure required to cause the flow may be less than the strength of the paste. If it is expelled, the displaced water must move toward the nearest air void, which is the one enclosed by the body of paste in question. In further developments we shall assume that the conditions may either be such that the water may be expelled without rupturing the paste or be such as to produce rupture.

The paste around the bubble will be regarded as being composed of spherical shells of thickness Δr. The volume of any one of these elements will be $4\pi(r')^2\Delta r'$, where r' = distance from the particular element to the center of the bubble[3]

Let the amount of water expelled from the element on freezing be Δv. Then,

$$\Delta v = (1.09 - 1/s)\Delta w_f 4\pi(r')^2\Delta r'$$

where Δw_f = increment of water frozen, g per cc of paste,

s = saturation coefficient,[4] which is the ratio of the amount of capillary water present to the capillary porosity, ϵ.

Notice that when $s = 1$, $1.09 - 1/s = 0.09$, which is the normal expansion from freezing 1 g. of water. When the paste is not saturated, the effect is considered to be the same as reducing the expansion coefficient of the water in a saturated paste.

Since the amount of water frozen is a function of temperature, so also is the amount expelled. That is,

$$\frac{dv}{d\theta} = (1.09 - 1/s)\frac{dw_f}{d\theta} 4\pi(r')^2\Delta r' \qquad (1)$$

where θ = temperature $\times(-1)$ C.

The rate of efflux from the element will be

$$\frac{dv}{dt} = (1.09 - 1/s)\frac{dw_f}{d\theta}\frac{d\theta}{dt} 4\pi(r')^2\Delta r', \qquad (2)$$

where t = time in seconds and $\frac{d\theta}{dt}$ = rate of cooling.

A volume element (shell) at distance r from the center of the bubble must transmit all the increments of water displaced from elements

[2] The final melting point is the highest temperature at which ice can exist in the concrete ((*6*), p. 933).

[3] See final pages for a summary of nomenclature

[4] Throughout the ensuing discussion the degree of saturation of the paste is under consideration, rather than the degree of saturation of the concrete as a whole It is believed that, as a rule, entrained-air concrete does not become saturated If under any circumstance it does, the paste will have reached saturation long before the concrete as a whole (*2*, *3*).

between it and the limit of the "sphere of influence." Hence, the total efflux at r will be

$$\frac{dV}{dt} = (1.09 - 1/s)\frac{d\theta}{dt}\frac{dw_f}{d\theta}4\pi\int_r^{r_m}(r')^2\,dr' \quad (3)$$

where r_m = radius of "sphere of influence," and V = total efflux through a given volume element.

The area through which this flow takes place $= a = 4\pi r^2$. Then, on integrating Eq. 3 and dividing by $4\pi r^2$ we obtain

$$\frac{dV}{dt}\frac{1}{a} = C\left(\frac{r_m^3}{r^2} - r\right) \quad (4)$$

where

$$C = \frac{1}{3}(1.09 - 1/s)\frac{d\theta}{dt}\frac{dw_f}{d\theta} \quad (5)$$

The resistance to motion of water through the paste must give rise to a hydraulic-pressure gradient. By Darcy's law

$$\frac{dP}{dr} = \frac{\eta}{K}\frac{dV}{dt}\frac{1}{a} \quad (6)$$

where P = hydraulic pressure, dynes per cm.^{2},
K = coefficient of permeability of the paste, sq. cm.,
η = coefficient of viscosity of water.

Combining Eqs. 4 and 6 we obtain

$$\frac{dP}{dr} = \frac{\eta}{K}C\left[\frac{r_m^3}{r^2} - r\right]. \quad (7)$$

Hence, integrating over the thickness r_b to r, we obtain

$$P = \frac{\eta}{K}C\int_{r_b}^{r}\left[\frac{r_m^3}{r^2} - r\right]dr$$

$$= \frac{\eta}{K}C\left[\frac{r_m^3}{r_b} + \frac{r_b^2}{2} - \frac{r_m^3}{r} - \frac{r^2}{2}\right] \quad (8)$$

This is a general expression for the hydraulic pressure at any point in the sphere of influence. We are interested in the maximum pressure, which will be at $r = r_m$, the outer boundary of the sphere of influence. Thus,

$$P_{max} = \frac{\eta}{K}C\left[\frac{r_m^3}{r_b} + \frac{r_b^2}{2} - r_m^2 - \frac{r_m^2}{2}\right]. \quad (9)$$

Let L = distance from bubble boundary to boundary of sphere of influence. Then

$$L = r_m - r_b \quad (10)$$

Using Eq. 10, we may reduce 9 to

$$P_{max} = \frac{\eta}{K}C\,\phi(L) \quad (11)$$

where

$$\phi(L) = \frac{L^3}{r_b} + \frac{3L^2}{2}.$$

If the paste is saturated, so that $s = 1$, then (see Eq. 5),

$$C = 0.03\frac{d\theta}{dt}\frac{dw_f}{d\theta},$$

and Eq. 11 becomes

$$P_{max} = \frac{0.03\eta}{K}\frac{d\theta}{dt}\frac{dw_f}{d\theta}\phi(L). \quad (12)$$

We may simplify the notation by letting

$$R = \frac{d\theta}{dt}$$

$$u = \frac{dw_f}{d\theta}.$$

Thus, for a paste that is not saturated we may write, from Eqs. 5 and 11,

$$P_{max} = \frac{\eta}{3}(1.09 - 1/s)\frac{uR}{K}\phi(L). \quad (13)$$

For a saturated paste,

$$P_{max} = 0.03\eta\frac{UR}{K}\phi(L). \quad (14)$$ [5]

[5] An earlier, mimeographed edition of this paper was given limited circulation. The earlier edition included a discussion based on the assumption that the permeability becomes smaller as freezing progresses because of the ice that forms during the period of flow. This discussion led to adopting an effective coefficient of permeability equal to $\frac{1}{10}$ the actual permeability of the paste. Since the earlier writing, new studies on the permeability of paste were completed. These studies indicated that the capillaries in which the ice forms are pockets isolated by layers of gel. The resistance to flow through the pockets is negligible compared with the resistance to flow through the barriers of gel. Since it is believed that ice does not form in the gel pores, it seems likely that

where U = the value of u when the paste is saturated, i e., when $s = 1.0$.

Expression for Permissible Bubble Spacing—From the hydraulic-pressure hypothesis it follows that for concrete of high frost resistance, the maximum intensity of hydraulic pressure must not be greater than the paste can stand without rupture. Moreover, for structures that have continuous access to moisture, such as many pavement slabs, the paste must be able to withstand the hydraulic pressure if it is frozen while completely saturated. Therefore, the expression for permissible bubble spacing will be developed on the basis of Eq. 14, that is, on the basis that $s = 1$.

Dividing Eq. 14 by the tensile strength of the paste, T, we obtain

$$\frac{P_{\max}}{T} = 0.03\eta \frac{R}{Z} \phi(L), \qquad (15)$$

where $Z = KT/U$. From information now at hand it seems that internal hydrodynamic pressure is effective over practically the whole cross-section of the paste (*4*, *5*). Therefore $P_{\max}/T$ must not exceed 1.0. Hence,

$$\phi(L)_{\max} = \frac{1}{0\,03\eta} \frac{Z}{R} \qquad (16)$$

The coefficient of viscosity η is a function of temperature and therefore changes during the period of water expulsion. However, inspection of the freezing curves shows that most of the capillary water freezes between 0 and −4C. Hence, we may adopt the value of η for −2 deg., or 0 019. poise. This gives

$$\phi(L)_{\max} = 1775 \frac{Z}{R} \qquad (17)$$

It will be seen that the parameter Z represents the properties of the paste. Hence, for a saturated paste, the maximum permissible value of L depends mainly on the properties of the paste and the rate of cooling.

Eqs 13, 14, and 17 apply only to a material in which the air voids are of the same size. Therefore, these theoretical equations would not be expected to hold exactly for a material in which the void-sizes cover a wide range. Nevertheless, we may expect the equations to give the correct order of magnitude of pressure intensity and permissible spacing.

Experimental Data—The foregoing analysis shows what the magnitude of hydrodynamic pressure will be when water is caused to flow in a porous material in a specified manner. This analysis should hold for any material containing interconnected pores. However, it tells us nothing specific about cement paste. To estimate the magnitude of pressures that may develop in hardened paste we must first turn to laboratory data and evaluate the parameter Z.

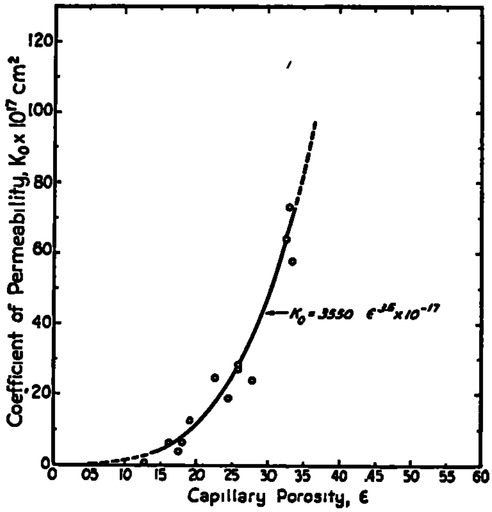

Figure 2. Coefficient of Permeability in Relation to Capillary Porosity for Air-Free Paste Made with Cement 15754

Data from which values of Z may be evaluated are available for six samples ((*6*), p. 933). The values of U were taken from curves of Figure 3. The coefficients of permeability were obtained from Figure 2 and the porosities of the respective samples. The tensile strengths were estimated from the gel-space ratios. (See Appendix.)

the effective permeability changes very little during the initial stages of freezing At least, the assumptions made previously as to the manner in which the ice might impede the flow no longer seem acceptable. Consequently, the present treatment is based on the permeability of the paste, without correction. Although the numerical results differ from those obtained earlier, the general significance remains as before

The curve for the coefficient of permeability K shown in Figure 2 represents the results of direct tests made recently in this laboratory.

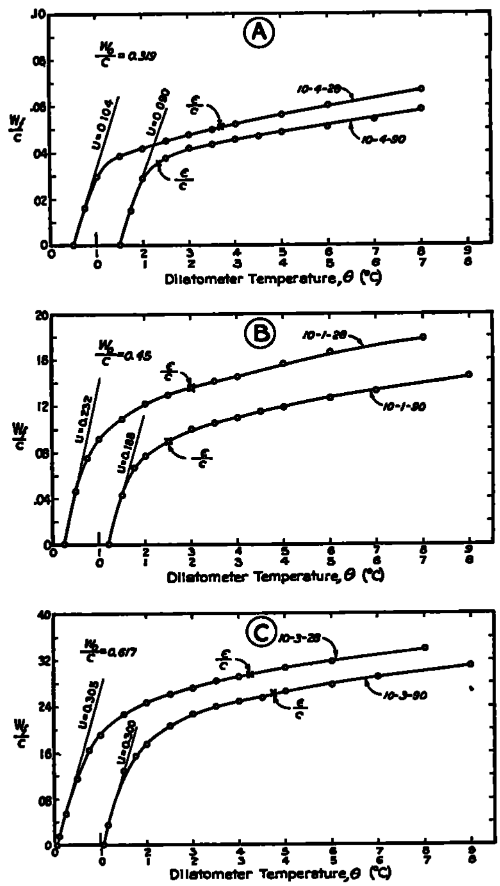

Figure 3. Melting Curves for Pastes of Three Different Water-Cement Ratios, Each at Two Different Ages. (Data from Ref. 6, p. 951)

Note: **These melting curves are considered to be the same as freezing curves under conditions that prevent supercooling. They are based on dilatometer measurements on saturated paste granules.**

Notice the differences in scale of ordinates.

ϵ/c designates the point where the amount of water frozen equals the capillary porosity.

Mixed in a vacuum, the pastes were completely free from entrained air. Over the range of data shown in the graph the relationship may be represented by

$$K = 3550\epsilon^{3\,6} \times 10^{-7} \Big]_{\epsilon = 0\,1}^{\epsilon = 0\,35}$$

This relationship was used for interpolation and short extrapolations.

The results of the calculations[6] are given in Table 1. The upper part gives the computation of parameter Z and the lower part, L_{max} for different *assumed* values of bubble radius, r_b.

It will be noted that these theoretical calculations indicate the distance L_{max} to be very small and to be different for pastes of different porosity. L_{max} varies also with the average bubble size, for a given value of $\phi(L)$,

TABLE 1

COMPUTATION OF L_{max} FOR SIX PASTES MADE FROM CEMENT 15754

A—Computation of Parameter Z

Ref No[a]	w_0/c	ϵ	$\Delta V_B / w_0$	Gel-Space Ratio	$K \times 10^{17}$ sq cm	$T \times 10^{-6}$ dynes per sq cm	U g per deg	$KT \times 10^{11}$	$Z \times 10^{10}$
10-4-28	319	081	84	0 90	0 4	63	104	25	24
10-4-90	319	051	90	0 94	0 1	69	090	7	8
10-1-28	450	177	70	0 83	7 0	52	232	364	157
10-1-90	450	118	80	0 88	1 7	59	.188	100	53
10-3-28	617	307	54	0 67	50 0	33	305	1650	540
10-3-90	.617	278	.58	0 71	34 0	37	300	1260	420

B—Computation of L_{max}

Ref No[a]	$Z \times 10^{10}$	$\phi(L)$		Computed L_{max}, *inches*		
		sq cm $\times 10^6$	sq in $\times 10^6$	$\alpha = 800$	$\alpha = 600$	$\alpha = 400$
10-4-28	24	1400	218	0 0078	0 0084	0 0090
10-4-90	8	500	78	0 0052	0 0055	0 0057
10-1-28	157	9200	1430	0 0158	0 0168	0 0180
10-1-90	53	3100	481	0 0106	0 0108	0 0123
10-3-28	540	31600	4900	0 0248	0 026	0 030
10-3-90	420	24600	3820	0 0226	0 024	0 028

$R = 3 \times 10^{-3}$ deg C per sec

$$\phi(L) = 1755 \frac{Z}{R} = 5\,85 \times 10^5 Z$$

$= 20$ deg F per hr

[a] The final number is the period of water-curing at 73 F, in days

the larger the size the larger the permissible spacing.

PART 2. OBSERVED PERMISSIBLE BUBBLE SPACING

The theoretical equations developed in Part 1 indicate that the maximum permissible spacing will differ according to differences in paste characteristics and to differences in rate of cooling. However, the equations ob-

[6] Figure 4 was constructed to facilitate the computations

tained are not sufficiently rigorous to provide reliable predictions of air requirements on the basis of calculations alone The equations for hydraulic pressure involve simplifying assumptions, and the computation for L_{max} will apply strictly only to pastes in which the air voids are equal in size. Therefore, the permissible spacing factor must be established empirically This will require an extensive program of tests.

To make experimental studies of maximum permissible bubble spacing, a means of determining distances void to void is necessary. One such means has been described by Verbeck (*7*). Another will be described here. Also, from data obtained in this laboratory, a tentative limit on the spacing factor, applicable to paving concrete, will be estimated.

Computation of a Spacing Factor Based on Linear Measurements—The spacing of air voids can be computed approximately from linear measurements on cross-sections of concrete—the traverse method of estimating air content of hardened concrete (*8*, *9*). By this method, measurements are made along a straight line across a plane section, the lengths of the chords across the bubble sections being measured cumulatively. The total length of such chords divided by the total length of the traverse is nearly equal to the volume fraction of air in the concrete. If during the course of this measurement the number of bubbles intersected by the line is recorded also, it is

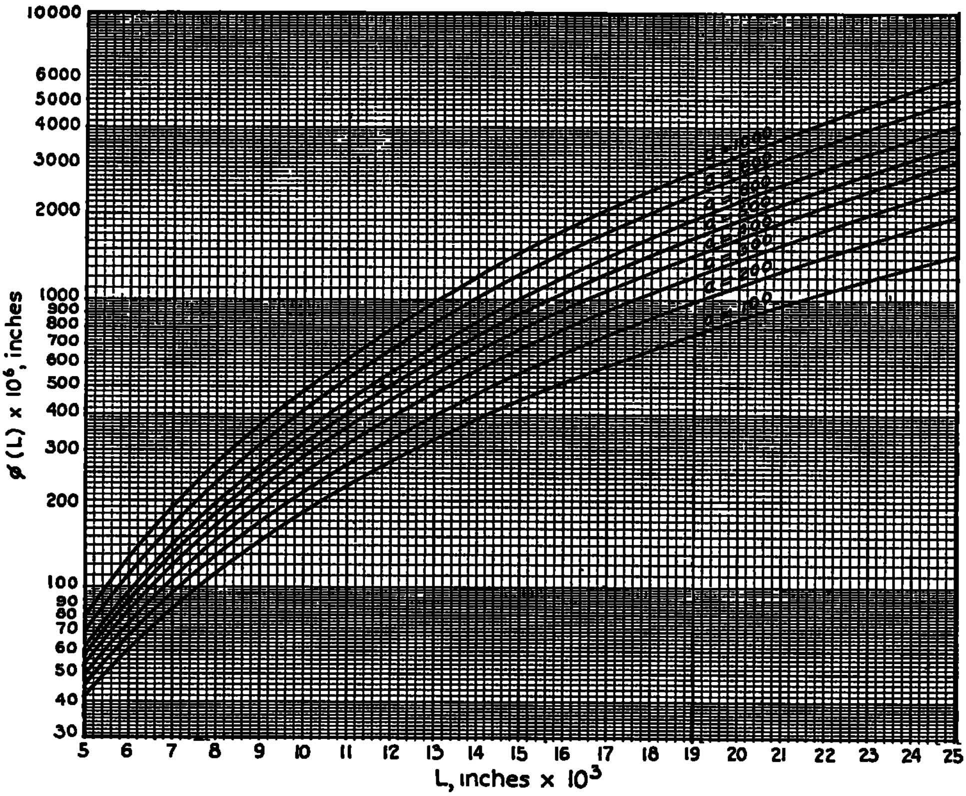

Figure 4. Relationship between $\phi(L)$ and L

$$\phi(L) = \frac{L^3}{r_b} + \frac{3L^2}{2}$$

then possible to compute a spacing factor, as will be described.

Let A = total volume of air voids, fraction of concrete volume,

n = number of voids intersected per unit length of traverse,

l = average distance across intersected voids along the line of traverse.

The relationship on which the linear traverse method of determining air content is based is

$$A = nl \tag{18}$$

T. F. Willis[7] has shown that regardless of the size-distribution of the voids, the specific surface of the voids, that is, the boundary area of the air-voids per unit volume of air, can also be determined from l. The relationship is simply

$$\alpha = \frac{4}{l} \tag{19}$$

where α = specific surface of air voids, boundary area per unit volume of air.

Hence, from Eq. 18,

$$\alpha = \frac{4n}{A}. \tag{20}$$

Void Spacing Factors—From the relationships just given, we can obtain a spacing factor of sorts simply by computing the volume of paste per unit area of void boundary. That is, if the paste content is p, the average thickness of the paste around the voids will be

$$\frac{p}{\alpha A} = \frac{p}{4n} \tag{21}$$

The result so obtained diminishes in accuracy as the ratio of the thickness of the paste layer (so computed) to the diameter of the void increases. It does not take into consideration the actual shapes of the paste-filled spaces between the spheroidal voids.

Another spacing factor may be obtained by assuming that the voids are equal-size spheres, each sphere having the same specific surface as the measured specific surface. The radius of this hypothetical sphere will be

$$r_h = \frac{3}{\alpha} = \frac{3}{4} l. \tag{22}$$

Thus we will deal with a hypothetical system in which the boundary area of the voids in the paste is equal to the actual boundary area, but we do not take into account the influence of the range in void sizes on the geometry of the paste webs between the voids.

To compute the spacing of the hypothetical bubbles just described, we regard each void as being at the center of a cube, the sum of the volumes of all such cubes and the enclosed void equaling the combined air and paste content of the concrete. The "sphere of influence" of each void as defined in Part 1 is the radius of spheres circumscribing the hypothetical cubes, which spheres overlap, except at cube corners The radius of the sphere of influence is equal to the half-diagonal of the cube.

The volume of a single hypothetical cube is

$$\frac{p + A}{N},$$

where p = paste content,

N = the number of hypothetical voids of radius r_h required to equal the actual air volume, A. (N is not the actual number of bubbles.)

Hence, edge-length of the hypothetical cube will be

$$\left(\frac{p + A}{N}\right)^{1/3}.$$

Therefore,

$$r_m = \frac{\sqrt{3}}{2}\left(\frac{p + A}{N}\right)^{1/3} \tag{23}$$

where r_m = radius of circumscribed sphere, the "sphere of influence,"

and $\frac{\sqrt{3}}{2}$ = ratio of half-diagonal to edge-length.

[7] After reviewing an earlier draft of this paper, T. F. Willis, Research Engineer, Missouri State Highway Department, prepared a rigorous analysis of this problem, using the mathematics of probability. This revealed certain errors in the earlier draft The author is greatly indebted to Mr Willis for his contribution. See discussion of this paper by T. F. Willis.

The spacing factor L is equal to the difference between the radius of the sphere of influence, r_m, and the radius of the bubble: that is,

$$L = r_m - r_b.$$

Therefore,

$$L = \frac{\sqrt{3}}{2}\left(\frac{p + A}{N}\right)^{1/3} - r_b. \qquad (24)$$

By definition

$$N = \frac{A}{\frac{4}{3}\pi r_b^3} = \frac{\alpha^3 A}{36\pi} \qquad (25)$$

Hence, from Eqs. 24 and 25,

$$L = \frac{3}{\alpha}\left[1 4\left(\frac{p}{A} + 1\right)^{1/3} - 1\right] \qquad (26)$$

On comparing Eqs. 21 and 26 we find that

Item		Aggregate		Air Content A, *percent*	No of Voids per inch, n	Specific Surface of Voids, $\alpha = 4n/A$	r_b in thousandths of an inch	Paste Content of Concrete p, %	Computed Spacing Factor, *inches*	
		Fine	Coarse						Eq. 21	Eq. 26
1	CA-2	Elgin	Limestone	2.2	4.95	900	3 32	22 9	.0115	.0072
2	CA-4	Elgin	Slag	5.2	11.40	876	3.42	23 3	.0051	0050
3	CA-6	Elgin	Elgin	8.1	14 30	706	4.25	22 0	.0038	.0049
4	CA-7	Elgin	Trap Rock	1.8	1.83	406	7.40	26.2	.0358	.0185
5	CA-8	Elgin	Trap Rock	4.7	6 43	546	5.50	24.5	.0095	.0086
6	352-5	Kan "Sand-Gravel"		4.4	1 10	100	30 00	29 6	0673	.053
7	352-6	Kan. "Sand-Gravel"		11.2	4 35	155	19 30	26 9	.0155	.023
8	352-17	Kan. "S-G" + Limestone		1.3	0 29	89	33 70	27.9	.24	.099
9	352-18	Kan. "S-G" + Limestone		8.7	7.33	337	8 90	24 5	.0084	.0106

TABLE 2
DATA ON AIR CONTENT AND SPACING FACTORS FOR VARIOUS KINDS OF CONCRETE

when $p/A = 4.33$, the computed factors are equal; when p/A is greater than 4.33, Eq. 26 gives the smaller factor, and vice versa. There is reason to believe that the factors obtained from either equation exceed the actual spacing. Therefore, it would seem permissible to use Eq. 21 for the low range and Eq. 26 for the high range. For average air-entrained concrete, p/A is generally above 4.33; hence the use of Eq. 26 is indicated for most cases.

Air Requirement in Terms of Specific Surface of Air Voids—If the void spacing in concrete of high frost resistance must be limited to some maximum distance corresponding to L_{max}, the air requirement will depend on the specific surface of the voids and on the paste content. The relationship needed is obtained by solving Eq. 26 for A. The result is

$$A = \frac{p}{0.364\left[\frac{\alpha L_{max}}{3} + 1\right]^3 - 1} \qquad (27)$$

We may therefore conclude that the higher the specific surface of the voids, the smaller the air requirement—provided that A always exceeds the possible total expansion of the freezable water.

Results of Measurements—Measurements of air by the traverse method are now under way in this laboratory. Some results are given in Table 2. The concretes represented in the upper groups were from a series made in the laboratory with different types of coarse aggregate. The concretes in the lower group were some of those reported on by Klieger (*10*)

The wide range in bubble-size distribution among these concretes is indicated by the differences among their specific surfaces. Notice that the maximum α is about ten times the minimum.

A comparison of items 1 and 4 of Table 2 is of special interest. These represent identical mixes except for the type of coarse aggregate. Also, they have practically identical air contents. The specific surface of the voids is 900 for item 1 and 406 for item 4. The spacing factors differ by a factor of 2.5.

It is instructive also to compare item 3 with item 9. Here the air contents are high and about equal, but the spacing factor of item 9 is twice that of item 3.

In Part 3 it will be shown that such differences in void size are responsible for very large differences in air requirement.

Tentative Estimate of Permissible Spacing Factor—From data at hand it is possible to estimate the maximum permissible spacing factor for concrete able to withstand a freezing and thawing test employing a 20 F. per hour cooling rate. This estimate is necessarily tentative since very few freezing-and-thawing-test data are available for which specific surface as well as air content is known.

Gonnerman (*11*) found the air requirement to be about 3 percent for a considerable variety of concretes. Although the bubble sizes for these concretes are not known, recent measurements made in this laboratory indicate that the calculated specific surface of the air voids, α, would average about 600 sq. in. per cu. in. (r_h = 0.005) when the air content is 3 percent, excepting unusual concretes such as the Kansas "sand-gravels." The paste content was close to 0.27. Using these values in Eq. 26, we obtain,

$$L = 0.005\left[1.4\left(\frac{0.27}{0.03}+1\right)^{1/3} - 1\right] = 0.010 \text{ in}$$

Thus, it is estimated that among those specimens able to withstand the freezing test with an air content of 3 percent, the spacing factor is about 0.010 in. or less.

The specimens tested by Gonnerman had been water-cured for 14 days, dried in laboratory air for 1 month, stored over water in a closed container for 2 months or more, and finally were soaked in water for 7 days before beginning the test The cements may therefore have been at a fairly advanced stage of hydration. The water-cement ratio was about 0.45 by weight. Therefore, with respect to w/c and curing time the specimens were comparable with Ref. 10-1-28 or perhaps 10-1-90 of Table 1. Whether they were also comparable with respect to parameter Z is not known, for the cements were not the same. But it seems likely that among these specimens Z would fall within the range 50 to 500 for which the theoretical values of L_{max} (Table 1) for small voids range from 0.0106 to 0.026 in. We should expect Z to be close to the lower of these limits. Thus the estimate based on Gonnerman's data, 0.010 in., is in general, though not exact, agreement with the theoretical values of Table 1.

On the basis of these general indications it is tentatively concluded that paving-type concrete should withstand the particular freezing and thawing test used in this laboratory if the spacing factor is not over 0.01 in. for voids of the usual specific surface.

PART 3. DISCUSSION

Eq. 13[8] is an expression of the hydraulic-pressure hypothesis concerning the mechanism of the action of frost on the paste in hardened concrete. When experimental values for the properties of the paste and the rate of cooling and degree of saturation of the paste are inserted, it purports to give the intensity of hydraulic pressure that will develop in any given very small region in the paste.

Eq. 17 gives a factor related to the maximum thickness of a body of paste that can be frozen while saturated without developing hydraulic pressures exceeding the tensile strength of the paste. This theoretical factor—the permissible bubble spacing factor, L_{max}—is remarkably close to the values estimated from direct measurements This agreement is regarded as strong support to the hydraulic-pressure hypothesis. The closeness of agreement is not the crucial test of the hypothesis, however. Admittedly, the derivation of the basic equations for hydraulic pressure and for the spacing factor are not rigorous; therefore, the indication of quantitative agreement is spurious to some degree. The outstanding significance of the analysis is that it accounts for the necessity of closely spaced voids in paste liable to be frozen rapidly while it is saturated, or nearly saturated, with water; the order of magnitude of the calculated requirement is the same as the actual requirement It is especially significant that the computation of permissible bubble spacing involved the use of experimental values for certain properties of the paste, particularly permeability, strength, and freezable-water coefficient. The magnitudes of these experimental values, as well as the theory as to their combined effects, determined the magnitude of the computed result.

The computations based on measured properties of the paste show that a body of nearly saturated paste more than a few hundredths of an inch thick cannot possibly be frozen rapidly without incurring damage.

[8] A summary of principal equations is given at the end of the paper.

This indication of the equation is in agreement with experiments showing that concrete of good quality is almost destroyed by one freezing if the paste is first thoroughly saturated There seems to be little basis for doubting that the life of any part of a non-air-entrained concrete member subjected to freezing and thawing in the presence of external water is, so far as the paste is concerned, limited to the length of time required for the paste in that part to become saturated or nearly so However, to reiterate, Eq. 13 and laboratory data indicate that if the maximum distance through the paste, void to void, is limited to some very small value, apparently 0.02 in. or thereabouts, the paste will suffer only nominal damage from freezing. At least this appears to be true for pastes in which the hydration products more than half fill the originally water-filled space. No data are available for pastes of higher capillary porosity.

Relation of Air Requirement to Paste Characteristics—According to Eq 27 the air requirement depends principally on the specific surface of the voids and the maximum permissible spacing factor[9] By Eq. 17, we see the value of the spacing factor for saturated paste is dependent on the rate of cooling and the parameter Z, the latter representing the physical characteristics of the paste. Hence, for a given cooling rate, air requirement depends principally on the specific surface and parameter Z.

Z depends only on the degree to which the originally water-filled space in the paste is filled with hydration products, at least for a given cement cured under standard conditions. Although the data now available are not extensive, they indicate that differences in water-cement ratio and extent of hydration are important only to the degree to which they influence Z[10] Therefore, Z can be used to represent the paste characteristics that are involved in this discussion

An empirical relationship between Z and the extent of hydration is given by the curve in Figure 5. The values of Z are shown in relation to $\Delta V_B/w_0$, where ΔV_B is the increase in the volume of solids due to hydration and w_0 is the volume of originally water-filled space. Capillary porosity, which is equal to the residue of originally water-filled space, diminishes to zero as $\Delta V_B/w_0$ approaches unity.

The trend of the curve through the points is such that Z seems to approach zero as the capillary porosity approaches zero (that is, as the originally water-filled space becomes completely filled with hydration products).

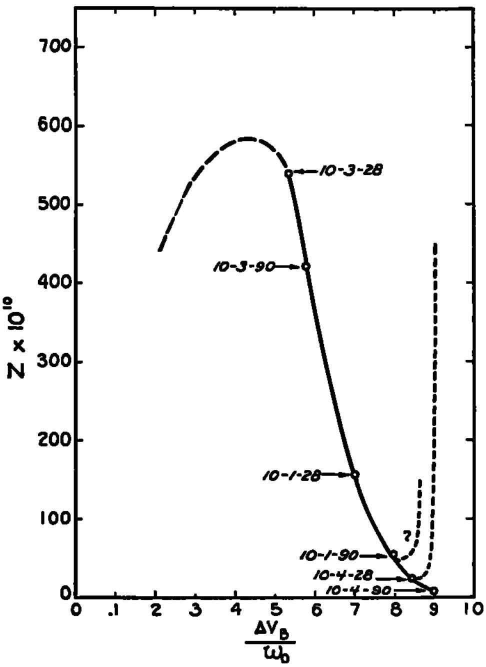

Figure 5. Relationship of Z to Extent of Filling of Originally Water-Filled Space

The implication of such a trend is that a paste without capillary pores has an air requirement of infinity for protection of the saturated paste This would mean that such pastes would be unable to stand the freezing and thawing tests with any amount of entrained air, whereas the fact is that such pastes withstand freezing indefinitely without the aid of any entrained air. Moreover, from the make-up of parameter Z

$$Z = \frac{K_0 T}{U}$$

[9] Paste content is not an important variable except where differences in maximum size of aggregate are involved

[10] This matter is now under study in this laboratory

it is clear that it must become infinite—not zero—because as the capillary porosity approaches zero the freezable water and hence U approaches zero while permeability K_0 and tensile strength T remain finite. The only question concerns the point at which the curve begins to turn upward.

The data contain internal evidence that the curve turns upward before it gets to experimental point 10-4-90. A study of Figure 3 brings out the facts given in Table 3. Notice that for all but 10-4-90 the initial slopes of the melting curves were established while about half the capillary water was still unfrozen. In this one case the amount of freezable water was very small and 86 percent of it froze during the first half degree drop. It is probable that most of this water froze in

TABLE 3

Ref No.	ϵ/c	Temperature[a] at Which Curve Departs from Initial Tangent	Percentage of Capillary Water Frozen at That Temperature
10-4-28	051	−0 40	47
10-4-90	035	−0.50	86
10-1-28	135	−0 35	44
10-1-90	090	−0 40	51
10-3-28	287	−0 50	42
10-3-90	.260	−0 50	39

[a] Degrees of temperature below final melting point

place, because of dilation of the paste rather than expulsion of water from the paste.[11] Therefore U of parameter Z, which is supposed to represent the amount of water expelled per degree drop in temperature, could easily be zero in such pastes and thus the curve could sweep upward about as shown. Possibly the point of departure from the locus of the plotted points is still farther to the left, that is, at a higher degree of capillary porosity, but the present data contain no clear evidence to this effect.

It is significant that the value of Z decreases as the originally water-filled space becomes filled with hydration products, that is, as the capillary porosity diminishes This is true within limits. One limit has already been discussed; it is the point where the freezable water coefficient U approaches zero and the curve is thereby caused to turn upward. The indication of the present data is that this limit is found where the space is about 80 to 90 percent filled with hydration products, but, as said before, the point cannot be established without further experimental studies.

The existence of a limit at a lower value of $\Delta V_B/w_0$, that is, at a higher capillary porosity, can only be surmised since unfortunately data are not available for pastes in which the original space is less than half filled with solids.[12] It seems certain, however, that the curve should not continue its upward trend indefinitely. From the make-up of parameter Z we see that K_0 would approach the permeability of the fresh paste as a limit; U would approach a maximum value depending on the original water content and on the electrolyte concentration; and T, the tensile strength, would approach that of the fresh paste, practically zero. Therefore, Z would be very small in pastes having high capillary porosity. The curve must find a maximum and descend possibly as indicated by the leftward extension of the curve.

It is probable that when $\Delta V_B/w_0$ is very small the theory on which this discussion is based does not apply at all. As shown by McHenry and Brewer (*5*), ice segregation on a macroscopic scale takes place if concrete is frozen when 4 hr. old. At what stage of hydration or degree of space-filling this phenomenon ceases to appear has not been determined, but it apparently ceases before the paste has become half filled.

Thus the indication of the curve is that for concretes exposed to water for long periods, the air requirement becomes progressively greater as hydration proceeds; but the paste may, if it is rich enough, finally become immune to frost action through the "curing out" of all freezable water. For continuous exposure to moisture the present indications are that the paste having the highest air

[11] The melting curves were established by dilatometer measurements on small granules of saturated paste Either expulsion of water or dilation of the granule would be registered by the dilatometer reading.

[12] Such pastes would be either those with water-cement ratios above 0 6 by weight, cured 28 days or more, or richer pastes cured for shorter periods (assuming an average Type I cement).

requirement is that in which the amount of cement is sufficient eventually to fill about 80 to 90 percent of the space but not enough to fill all the space.

We should note in passing that the relationship just discussed pertains to the theoretical requirements for preventing disruptive pressures caused by the freezing of capillary water. If these requirements are not met, we should expect the paste to fail, regardless of Z, except when Z is infinity. What the relative rates of disintegration would be among pastes having different values of Z cannot be told from those phases of the theory that are developed in this paper.

It would not be correct to assume that the rates of disintegration would be related to $\Delta V_B/w_0$ by a curve having the same shape as the Z curve. Under some circumstances, however, we might expect a paste having a high value of Z to show high resistance to frost action, whereas one with a lower capillary porosity and also a lower value of Z might show a considerably higher rate of disintegration. For example, if the two pastes were frozen at a low rate after a long period of curing, the void-spacing requirement of the paste with a high Z value might be met by that of the natural voids in the concrete, whereas at the same low rate of freezing the natural voids might not protect the paste having a low value of Z. Thus under this circumstance the poorer grade of concrete might show superior resistance to frost action. On the other hand, at a higher rate of freezing, with neither paste adequately protected, the specimen with a high Z might fail more rapidly than the denser specimen having a lower value of Z, and thus the poorer grade of concrete would show the higher rate of disintegration.

It is evident that a considerable amount of laboratory study must be completed before all the implications of these relationships can be fully understood.

Theoretical Relationship between Air-Requirement and Specific Surface of Voids—With the value of Z known from laboratory measurements on a given paste, the spacing requirement in terms of $\phi(L)_{max}$ can be computed from Eq. 17. However, a value thus obtained could be considerably different from the true value because of the nature of the assumptions made in arriving at the numerical coefficient in Eq. 17. In other words, we do not regard Eq. 17 as suitable for establishing L_{max} for a given paste, until after the numerical coefficient in that equation has been established empirically.

Let us suppose that from laboratory experiments we have found the maximum permissible spacing factor, $\bar{L}_{max}$,[13] to be 0.01 in. with α at 600 sq. cm. per cu. in. We wish to determine what the spacing factors will be, and ultimately what the air-requirements will be, for concretes containing the same kind of paste but air of different specific surface. The problem is thus that of establishing spacing factors that will limit the hydraulic pressure to the same maximum when factors other than specific surface are equal.

From Eq. 15 we see that pressure is related directly to $\phi(L)$ rather than to L. Therefore, having found that $\bar{L}_{max}$ is 0 01 in. under specific conditions, we must find the corresponding $\phi(L)$ before making further calculations.

TABLE 4
SOLUTIONS OF EQ 27 FOR THE CONDITION
$\phi(\bar{L}) = 350 \times 10^{-6}$ SQ IN

Spec Surf of Voids, alpha *sq in per cu in*	$\bar{L}_{max}$ *in*	Computed Air Requirement for Paste Content Indicated, *percent*			
		Neat	40%	27%	20%
800	0094	6 80	2.72	1 84	1 36
600	0100	11 33	4 53	3 06	2 27
500	0104	15 6	6 24	4 21	3 12
400	0108	23 3	9 32	6.29	4 66
300	.0114	38.9	15 56	10 50	7.78

This may be done readily by means of Figure 4. We note that if $L = 0.01$ in when $\alpha = 600$, $\phi(L) = 350 \times 10^{-6}$ sq. in. Values of $\bar{L}$ for other values of α are given in columns 1 and 2 of Table 4.

With corresponding values of α and $\bar{L}$ thus established, we may calculate air requirement from Eq. 27. The results of such calculations are given in the last four columns of Table 4.

The paste percentages correspond roughly to mortar, paving concrete and mass (cobble) concrete, respectively. The values of specific surface cover the range found so far among air-entrained concretes.

The sensitivity of air requirement to specific surface of the voids is very apparent in Table 4. Considering a concrete with 27 percent paste, we see that the air requirement ranges from less than 2 to more than 10 percent.

[13] L_{max} denotes a theoretical value using Eq. 17; $\bar{L}_{max}$ denotes an empirically determined value, using Eq. 26 for computing the factor.

In this connection we may recall that the spacing factors computed from Eq 27 probably become progressively more in error as the air content increases; the computed values will become progressively greater than the actual values. Hence, we may expect the actual influence of a decrease in the specific surface, α, to be somewhat less than is indicated by the figures given in Table 4. The real relationship is yet to be established by suitable laboratory experiments.

Critical Degree of Paste Saturation—By Eq. 15, the ratio of hydraulic pressure to tensile strength is

$$\frac{P_{max}}{T} = 0.03\eta \frac{R}{Z} \phi(L) \quad \text{(Eq 15)}$$

Let us suppose that $\phi(L)$, R, and Z are such that when the paste is frozen while saturated, P exceeds the tensile strength, T. If the paste is not saturated, the pressure may not exceed the strength. For the unsaturated state Eq. 13 applies, i.e.,

$$P_{max} = \frac{\eta}{3}(1.09 - 1/s)u \frac{R}{K} \phi(L) \quad \text{(Eq 13)}$$

However, u, the freezable water coefficient, is not independent of s, the degree of saturation of the paste. It becomes smaller as s becomes smaller. At present, experimental data for the relationship are not available. It will suffice for the present purpose to estimate a value from the known value of u for the saturated state. We assume that the relationship is a linear one such that when $s = 1$, $u = U$ and when $s = 0.917$, $u = U/2$.

These conditions are satisfied by the expression

$$u = \frac{s - 0.834}{0.166} U$$

Substituting these values in Eq. 13, we obtain

$$P_{max} = \frac{\eta}{3} \phi(s) \frac{UR}{K} \phi(L) \quad (28)$$

where

$$\phi(s) = (1.09 - 1/s) \frac{s - 0.834}{0.166} \quad (29)$$

The relationship between $\phi(s)$ and s is given in Figure 6. It shows that when s = 0.917, $\phi(s)$ = zero and when s = 1.0, $\phi(s)$ = 0.09. Thus, for a given concrete the hydraulic pressure may vary from zero to the maximum determined by other factors.

Figure 6 shows that very small changes in the degree of saturation of the paste produce large effects on the intensity of hydraulic pressure generated by freezing. For example, when s = 0.99, the hydraulic pressure indicated is about 86 percent of what it should be if the paste were saturated; at s = 0.98, the relative pressure is 68 percent; at s = 0.97, 56 percent. Although these figures are not to be regarded as quantitatively exact, it is

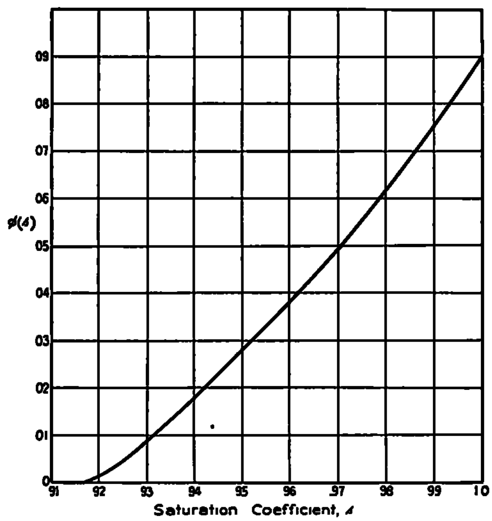

Figure 6. Relationship between $\phi(s)$ and Degree of Saturation (s)

clear that a relatively slight desiccation of the paste may serve to prevent failure due to freezing of the paste when the void spacing is too great.

The internal drying of the paste that accompanies the reactions between cement and water, which has been called self-desiccation ((*6*), p. 986), is known to be an important factor in frost resistance. The figures just given show that the degree of desiccation need not be very great. Notice that if s drops to 0.917, P_{max} becomes zero.

As already indicated, if the air voids are too widely spaced, the value of P_{max} will exceed the tensile strength of the paste if s has some value between 0.917 and 1 0. That is, at some particular value of s

$$\frac{P_{max}}{T} = 1 = \frac{\eta}{3}\phi(s)_{crit}\,\frac{UR}{TK}\phi(L)_c$$

and

$$\phi(s)_{crit} = \frac{3Z}{\eta R\phi(L)_c} \qquad (30)$$

In this equation $\phi(L)_c$ is any value of $\phi(L)$ giving $P_{max}/T \leq 1\,0$ with s equal to 1.0. For such spacing factors, the critical value of the paste-saturation factor depends on the rate of freezing and the paste properties represented by Z

Effect of Extent of Hydration on Critical Saturation Degree—Consider a paste at different stages of hydration, taking the data from Table 1:

	w_0/c	Age	$Z \times 10^{10}$
Paste No. 1 (10-3-28)	0 617	28d	540
Paste No 2 (10-3-90)	0 617	90d	420

Since both items represent the same paste but at different ages the spacing factor is the same for both. Suppose it is such that at a given rate of freezing No 1 fails rapidly when $s = 0.99$. Then, by Figure 6, $\phi(s)_1 = 0\,078$. At what degree of saturation should No. 2 fail? By Eq 30,

$$\frac{\phi(s)_2}{\phi(s)_1} = \frac{Z_2}{Z_1} = \frac{420}{540} = 0\,8.$$

Therefore, $\phi(s)_2 = 0.8, \phi(s)_1 = 0.8 \times 0.078 = 0.0625$, and from Figure 6, $s_2 = 0.98$.

For the extreme differences in Z indicated in Figure 5, we find

$$\frac{\phi(s)_2}{\phi(s)_1} = \frac{50}{600} = 0.083$$

Hence, $\phi(s)_2 = 0\,083 \times 0\,078 = 0\,0065$
and $s_2 = 0.925$, by Figure 6.

Thus, it follows that at the same stage of hydration (not necessarily at the same age) the critical degree of saturation may be lower for rich pastes than for lean ones

Effect of Rate of Cooling on Air Requirement—Suppose that for a particular kind of concrete the permissible spacing factor is 0.01 in. when the rate of cooling is 20 F. per hour. For other rates of cooling the permissible spacing will not be the same According to Eq. 17,

$$y = \frac{20}{R}x \qquad (31)$$

in which $y = \phi(\bar{L}_{max})_R$ for freezing at R deg. F. per hr
$x = \phi(\bar{L}_{max})$ for freezing at 20 deg. F. per hr.
R = actual rate of freezing.

For a rate of 20 F per hr, we find in Figure 4 that $x = 350 \times 10^{-6}$ sq. in. Therefore,

$$y = \frac{350 \times 10^{-6} \times 20}{R} = \frac{0\,007}{R} = \phi(\bar{L}_{max})_R$$

Solutions for $(\bar{L}_{max})_R$ from these equations for various rates of cooling are given in Table 5. The corresponding air requirements ($\alpha = 600$) calculated from Eq. 27, are given also, assuming a paste content of 27 percent

TABLE 5

Rate of Cooling *deg F per hr*	$\phi(\bar{L}_{max})_R \times 10^6$	$(\bar{L}_{max})_R$	Computed Air Requirement
			percent
5	1400	0 017	0 9
10	700	0 013	1 7
20	350	0 010	3 1
50	140	0 007	6 7
100	70	0 0053	12 3

Apparently, all who have investigated the effect of rate of cooling have found that the severity of the test increases with increase in cooling rate The figures given in Table 5 are in qualitative agreement with such findings.

Notice also the indication that if the rate of cooling is very low, the total volume of entrained air, rather than the bubble spacing, may be the limiting factor. However, as will be seen below, the specific surface tends to decrease as the air content is reduced and therefore the air requirement may not become as low as the computations in Table 5 indicate.

It is of considerable interest that at freezing rates above 50 F. per hour, the computed air requirement is above that normally used in practice Therefore, when high freezing rates are used, air-entrained concrete gradually disintegrates. This accounts for the trend toward using very high cooling rates in freezing and thawing tests of air-entrained concrete.

Different experimenters have found that to destroy air-entrained concrete, such rates are necessary. They feel that only by destroying the specimens can they "bring out the differences" between the specimens. To the author, the practical significance of the differences thus developed seems very questionable.

Estimation of Air Requirement for Slow Freezing from Air Requirement for Fast Freezing—According to this hypothesis freezing disrupts the paste only when the hydraulic pressure generated by freezing exceeds the tensile strength of the air-free webs of paste between the air bubbles. To maintain maximum possible strength the air content should be no higher than is necessary to assure the prevention of pressures that exceed the strength of the paste. But if the air requirement is based directly on the ability of a specimen to withstand some of the tests now in use, the indicated air requirement would be much higher than it need be.

For example, some freezers employ cooling rates (measured at the center of a specimen) as high as 100 F. per hour (*12*).[14] Obviously, this is much higher than the natural cooling rates since even the air temperatures do not fall that rapidly in these latitudes.

According to the indications of these studies, tests employing high cooling rates should not be regarded as "accelerated" tests. They are actually overload tests, for they bring forces to bear that greatly exceed those that the material is expected to withstand, and thereby could lead to the use of unnecessarily high air contents.

It is possible, however, that the air requirement could be reliably estimated from the results of rapid freezing tests. To determine the air requirement for a given concrete, specimens containing different amounts of entrained air would be prepared, the largest amount being considerably greater than the expected requirement. These specimens would be subjected to freezing and thawing, carefully controlling the cooling rate at a definite value.[14] Of course, measurements of air content and specific surface are required also.

The results should reveal some particular value of spacing factor at which frost resistance is practically as high as for smaller values. From the spacing factor so determined, the air requirement for a different rate of freezing could be calculated. The procedure would be as follows:

It would be necessary to know the specific surface of the air at the air content giving the spacing factor desired. From the observed α and $(\bar{L}_{max})_1$, $\phi(\bar{L}_{max})_1$ would be obtained from Figure 4.

With the $\phi(\bar{L}_{max})_1$ corresponding to observed α and $\bar{L}_{max}$ thus established, it would be increased in proportion to the relative reduction in rate. For example, if $\phi(\bar{L}_{max})_1$ is based on a cooling rate of 50 F. per hour, the required $\phi(\bar{L}_{max})_2$ for 5 F. per hour would be 10 $\phi(\bar{L}_{max})_1$.

Then with $\phi(\bar{L}_{max})_2$ thus established, the air requirement could be calculated from Eq. 27 if the new specific surface was known or could be estimated.

To illustrate: Suppose that tests have been made using a freezer that cools at 50 F. per hour and that $\bar{L}_{max}$ has been found to be 0.007 in and $A = 6.7$ percent. We have found also that at 6.7 percent the specific surface is 600. We wish to determine the air requirement for the same concrete when that concrete is to be subjected to cooling rates not higher than 5 F. per hour. From Figure 4,

$$\phi(\bar{L}_{max})_1 = 140 \times 10^{-6} \text{ sq. in.}$$

Then

$$\phi(\bar{L}_{max})_2 = 50/5 \times 140 \times 10^{-6}$$
$$= 1400 \times 10^{-6} \text{ sq. in.}$$

For the same specific surface, $\alpha = 600$, $\phi(\bar{L}_{max})_2$ corresponds to $(\bar{L}_{max})_2 = 0.017$ (Fig. 4). If the new air requirement were computed on this basis, the result would be a low value, 0.9 percent. But if it is low, the assumption of constant α would probably not be warranted, for as the air content is reduced, α may decrease, and the computed 0.9 percent would be too low. Let us assume that in reducing the air content to 0.9 percent α is decreased from 600 to 330.[15] Then, by Figure 4, for the same $\phi(\bar{L}_{max})_2$, 1400×10^{-6}, the spacing factor $(\bar{L}_{max})_2$ would become 0.0197 in.

[14] This refers especially to the rate from about 32 to 28 F.

[15] These figures are selected from the one empirical relationship between α and A now at hand.

Hence, using these values in Eq. 27, we obtain,

$$A_2 = \frac{0.27}{0.364\left[\frac{(330)(0.0197)}{3} + 1\right]^3 - 1}$$

$$= 2.56 \text{ percent}$$

With the relationship between the air content and α for this concrete known, it could be observed that the assumed α either does or does not correspond correctly with the computed air requirement, 2.56 percent. Let us suppose that the experimental data show α actually to be 500 at 2.56 percent air. That will mean that our computed air requirement is too high. If it is lowered, α will be lowered also. Hence, we will assume the new value to be 420 and make a new estimate.

From Figure 4 (L_{max}) at $\alpha = 420$ and $\phi(L_{max}) = 1400 \times 10^{-6}$ is 0.0185. Thus,

$$A_2 = \frac{0.27}{0.364\left[\frac{(420)(0.0185)}{3} + 1\right]^3 - 1}$$

$$= 1.7 \text{ percent}$$

If the correspondence between A and α is still not close enough, the process could be repeated.

From the results shown in Table 5 it seems clear that there must be a practical limit of cooling rate above which indications of air requirement would be unreliable. At a cooling rate of 100 F. per hour the computed air requirement (at $\alpha = 600$) is about 12 percent. At such a high percentage nearly half the space interjacent to the aggregate particles is filled with air. It seems doubtful that normal requirements should be estimated from specimens containing such abnormally high air contents.

Limits to Application of Hypothesis—It is important to bear in mind that this paper deals with theoretical relationships. They seem worthy of attention because of the degree to which they are in agreement with data now at hand. Also, it deals only with the action of frost on the paste. If the aggregate is porous and water-laden, the aggregate, rather than the paste, may be the cause of disintegration. Also, stresses not due to hydraulic pressure may in some instances be the principal factor. It seems possible, however, that some failures of air-entrained concrete thought to be due to causes other than freezing may now be traced to conditions that produce entrained air of abnormally large mean bubble size.

SUMMARY OF PRINCIPAL MATHEMATICAL RELATIONSHIPS[16]

Relationship between function of spacing factor and the spacing factor:

$$\phi(L) = \frac{L^3}{r_b} + \frac{3L^2}{2}$$

Hydraulic pressure when the paste is not saturated:

$$P_{max} = \frac{\eta}{3}(1.09 - 1/s)\frac{uR}{K}\phi(L) \qquad \text{(Eq. 13)}$$

(See also Eq. 29)

Maximum hydraulic pressure developed by freezing saturated paste.

$$P_{max} = 0.03\eta\frac{UR}{K}\phi(L) \qquad \text{(Eq. 14)}$$

Ratio of maximum hydraulic pressure to tensile strength:

$$\frac{P_{max}}{T} = 0.03\eta\frac{R}{Z}\phi(L) \qquad \text{(Eq. 15)}$$

Maximum permissible value of $\phi(L)$:

$$\phi(L_{max}) = 1775\frac{Z}{R} \qquad \text{(Eq. 17)}$$

Specific surface of air-voids:

$$\alpha = \frac{4}{l}, \quad = \frac{4n}{A} \qquad \text{(Eq. 19 and 20)}$$

Void spacing factors:

$$L = \frac{3}{\alpha}[1.4(p/A + 1)^{1/3} - 1 \qquad \text{(Eq. 26)}$$

Air requirement:

$$A = \frac{p}{0.364\left(\frac{\alpha L_{max}}{3} + 1\right)^3 - 1} \qquad \text{(Eq. 27)}$$

[16] For key to symbols, see p. 200.

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NOMENCLATURE

a = area through which flow of displaced water takes place
A = air requirement or volume of air present, fraction of concrete volume
α = specific surface of air voids
c = weight of cement per unit volume of concrete
C = a parameter defined by Eq. 5
$\phi(L) = \frac{L^3}{r_b} + \frac{3L^2}{2}$
$\phi(L)_c$ = any value of $\phi(L)$ giving $P_{max}/T \leq 1.0$ when $s = 1$
ϵ = volume of capillary pores
η = coefficient of viscosity
f_c = compressive strength of concrete
f_p = compressive strength of neat cement paste
K = coefficient of permeability of paste
l = average chord length, i.e., the average distance across intersected bubbles along line of traverse
L = distance from bubble boundary to outer boundary of sphere of influence
$\bar{L}$ = computed spacing factor (Eq. 26);
$\bar{L}_{max}$ = computed or observed maximum permissible spacing factor
$\phi(\bar{L}_{max})$ = function of spacing factor, $\bar{L}_{max}$
n = number of voids intersected per unit length of traverse
N = number of hypothetical bubbles having radius r_h that would equal the actual air content of the concrete
p = paste content, sum of volumes of water and cement
P = hydraulic pressure
P_{max} = maximum hydraulic pressure
r = distance from any volume-element to the center of a bubble
r' = distance from a particular volume-element to the center of a bubble
$\Delta r'$ = thickness of volume-element
r_b = radius of air bubble
r_h = radius of hypothetical bubbles
r_m = radius of sphere of influence
R = rate of cooling, $\frac{d\theta}{dt}$
s = saturation coefficient
$\phi(s)$ = function of saturation coefficient. See Figure 6
t = time, in seconds
T = tensile strength of neat paste
T_c = tensile strength of the concrete
θ = temperature, degrees C., multiplied by -1
u = amount of water frozen per degree drop in temperature as given by the initial tangent to the melting curve, $\frac{dw_f}{d\theta}$, the "freezable water coefficient"
U = u when the paste is saturated
Δv = finite increment of water expelled from a volume-element on freezing
V = total efflux of displaced water through a given volume-element
ΔV_B = increase in volume of solids due to hydration
w_f = volume of water frozen
Δw_f = finite increment of water frozen
$\frac{dw_f}{d\theta}$ = initial tangent to the melting curve
w_n = weight of nonevaporable water
w_0 = weight of mixing water corrected for loss by bleeding
x = gel-space ratio
Z = a parameter representing physical properties of the paste: $\frac{KT}{U}$

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APPENDIX

Method of Estimating Tensile Strength—To use the theoretical equation for maximum permissible bubble spacing (Eq 16), it was necessary to estimate the tensile strength of the particular neat cement for which other data were available. Although briquet tests might have been made, this was not done because the result obtained is not considered to be true tensile strength.

Data were at hand from compression tests on 2-in. cubes of neat cement and mortar.

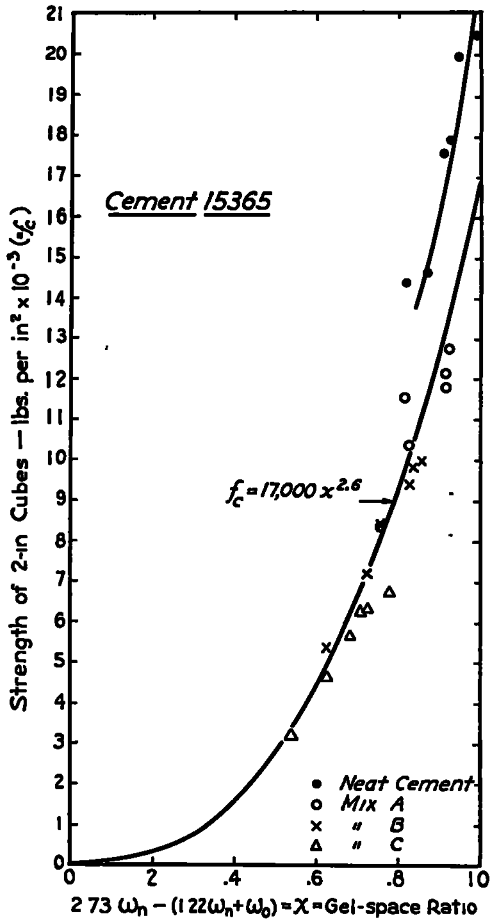

Figure 7. Strength Curves for 2-in. Cubes

These data are shown in Figure 7. The mortar data are fairly well represented by the equation

$$\text{cube strength} = 17{,}000x^{2.6} \text{ lb per sq. in.}$$

where

$$x = \frac{2.73\,w_n}{1.22w_n + w_0} = \text{gel-space ratio (Ref } 13)$$

The constants pertain to cement 15365 which was made from the same clinker as the cement dealt with in the text, No. 15754. The specific surfaces were slightly different.

The points representing neat cement cubes do not cover a wide enough range in gel-space ratio to establish a relationship. The curve drawn through the points corresponds to

$$\text{cube strength} = 22{,}000x^{2.6} \text{ lb. per sq in.}$$

It was assumed that this relationship would hold for compressive strength over the range of gel-space ratios needed, namely, $x = 0.67$ to $x = 0.94$.

Having thus established a relationship for neat cement cubes it was necessary to find some basis for converting compressive to tensile strength. A limited study of the literature on this controversial subject made it clear that whatever the result obtained, it would be open to criticism. Nevertheless, it was necessary to make some allowance for the length-to-thickness ratio of the cubes and for the relationship between tensile and compressive strength. For the length-to-thickness correction a factor of 0.85 was used, in accordance with ASTM C-42-44. On this basis we assumed that

$$f_p = 0.85(22{,}000x^{2.6}) = 18{,}700x^{2.6} \text{ lb. per sq. in.}$$

where

f_p = compressive strength of neat cement paste

To convert from compressive strength to tensile strength, the relationship found by Gonnerman and Shuman (*14*) was used. Their data show that up to a compressive strength of 2000 lb. per sq. in. the tensile strength of concrete is 10 percent of the compressive. From 2000 to 9000 lb. per sq. in., the latter figure being the upper limit of their data, the following relationship was found:

$$T_c = 100 + 0.057f_c,$$

T_c and f_c being the tensile and compressive strengths of the concrete. It was then assumed that this relationship would hold also for neat pastes This gave

$$T = 100 + 1066x^{2.6} \text{ lb. per sq in.}$$

or

$$T = (7 + 73x^{2.6}) \times 10^6 \text{ dynes per sq. cm.}$$

Thus, when $x = 1.0$, $T = 1166$ lb. per sq. in., or 80×10^6 dynes per sq. cm. The values needed for Table 2 were then computed as in Table 6.

TABLE 6

Gel-Space Ratio, x	$x^{2.6}$	$T \times 10^{-6}$ dynes per cm^2
0.67	0.361	33
0.71	0.410	37
0.83	0.616	52
0.88	0.717	59
0.90	0.760	63
0.94	0.852	69

These results are, of course, subject to considerable error. However, a large error in the estimate of tensile strength could be tolerated; the estimate of L_{max} would be near the observed value, even if T were doubled or halved. The shape of the curve in Figure 5 would be altered somewhat if the relationship between T and gel-space ratio is much different in form from the logarithmic relationship used; but even here, the correction would have to be very large to produce a significant change in the general indications of the analysis.

DISCUSSION

T. F. WILLIS, *Missouri State Highway Department*—Mr. Powers has presented an ingenious discussion of the magnitude of the hydraulic pressure developed during the freezing of concrete, and the relation between this magnitude and the factors controlling it. This relation, while admittedly theoretical, is sufficiently in accord with a number of known facts to make it worthy of consideration by all concerned with the problem of frost resistant concrete. Furthermore his development of the theory indicates the factors to be controlled or measured in laboratory tests designed to prove or disprove the theory. This in itself is a considerable forward step from the, shall we say, "mildly confused" present status of conducting freezing and thawing tests of concrete.

Among the factors indicated as having considerable effect on the hydraulic pressure developed is entrained air, together with certain characteristics of the bubble system of which it is composed. The following discussion pertains to Part 2 of the paper, which outlines a method of measuring, and equations for calculating, quantities which characterize the bubble system in any particular concrete analysed.

In one of the early drafts of the paper Mr. Powers stated his equations[1] (18) and (22) as they now are, but he defined $\bar{r}_A$ as the radius of the bubble having average volume.[2] Also he defined the N of Eq. (23) as the actual number of bubbles per unit volume of concrete, and attempted to relate it to $\bar{r}_A$ and A, the volume of air per unit volume of concrete. After some study it became evident that either $\bar{r}_A$, or N, or both were not properly defined. This raised doubts as to the validity of Eqs (18), (22), and (24), and the equation Mr. Powers then used to determine α, the specific surface of the air bubbles. As a result, the mathematical background of all these quantities and equations was analysed.

The errors (and it turned out that these may have been less vital than preliminary study indicated) have been corrected in the published version of the paper. However, the mathematical analysis presented herein gives the theoretical basis for a number of the equations; and as it applies to any system of spherical dispersoids being examined by the "linear traverse" method, it is offered with the hope that it may be of value to readers of the paper.

Preparation of a specimen of concrete for analysis by the linear traverse method exposes a number of sections of bubbles. In making the analysis, the bubble sections intersected by the traverse line are counted and the total length of chords intercepted by the sections is measured. Information is desired as to the air content per unit volume of concrete, a value expressive of the number of bubbles per unit volume of concrete, an average bubble radius, and the specific surface of the air bubbles. All the measured and desired quantities are dependent on, and hence functions of, the true diameters of the bubbles. However, geometric considerations make it obvious that the measured chord intercepts are generally not the same as the true bubble diameters; hence an expression relating the two quantities must be derived. If the bubbles of air entrained in concrete were uniform in size, the problem would be relatively simple; however, it is complicated by the fact that microscopic examination of aerated concrete indicates the bubble sizes to be distributed over a considerable range, and that nothing is known about the distribution function. Statistical methods are indicated for derivation of the desired relation.

MOMENTS OF STATISTICAL DATA

In the language of mathematical statistics, the arithmetic mean, $\bar{m}_A$, of a series of magnitudes m_1, m_2, m_3, etc, is the "first moment", $[m]_1$, of these magnitudes. That is, if there

[1] All equations numbered (31) or lower are identical with the similarly numbered equations of Mr. Powers' paper; equations derived in this discussion are numbered (32) and higher

[2] Mathematical symbols similar to those used by Mr Powers have the same significance he assigned to them, other symbols are defined as they are introduced. For convenience a list of symbols introduced in the discussion is appended

are n_1 magnitudes of value m_1, n_2 magnitudes of value m_2 etc., the arithmetic mean, or first moment, of the magnitudes is

$$\bar{m}_A = [m]_1 = \frac{n_1m_1 + n_2m_2 + n_3m_3 + \cdots n_im_i}{W} = \frac{\Sigma(nm)}{W} \tag{32}$$

where

$$W = n_1 + n_2 + n_3 + \cdots n_i$$

The second moment of the magnitudes is given by

$$[m]_2 = \frac{n_1m_1^2 + n_2m_2^2 + n_im_i^2}{W} = \frac{\Sigma(nm^2)}{W}$$

Similarly, higher moments may be obtained, as

$$[m]_3 = \frac{\Sigma(nm^3)}{W}$$

It is obvious that by method of calculation, l of Mr. Powers' paper is analogous to $[m]_1$, of Eq. (32), i.e. it is the first moment, or arithmetic mean, of the chord intercepts.

For a distribution of spherical bubbles of radii r_1, r_2, r_3, etc., each of the first three moments is related to a mean radius. The first moment, or arithmetic mean, is the magnitude which, multiplied by the total number of bubbles, will give a value equal to the sum of the true radii of all the bubbles, i.e.,

$$W[r]_1 = n_1r_1 + n_2r_2 + n_3r_3 + \cdot n_ir_i$$

$$\bar{r}_A = [r]_1 \tag{33}$$

The second moment produces a value which multiplied by 4π and the total number of bubbles, W, gives the total surface area of all the bubbles, i.e.,

$$S_T = 4\pi W[r]_2 \tag{34}$$

Since $\frac{S_T}{W}$ = the average surface area per bubble, and

$$\frac{S_T}{W} = 4\pi[r]_2 = 4\pi\bar{r}_s^2$$

where $\bar{r}_s$ = the radius of the bubble having average surface area,

then

$$\bar{r}_s = \sqrt{[r]_2}. \tag{35}$$

Similarly, the third moment yields a value which multiplied by $\frac{4\pi}{3}$ and the total number of bubbles, W, gives the total volume of all the bubbles,

$$V_T = \frac{4\pi}{3} W[r]_3 \tag{36}$$

Since $\frac{V_T}{W}$ = the average volume per bubble, and

$$\frac{V_T}{W} = \frac{4\pi}{3}[r]_3 = \frac{4\pi}{3}\bar{r}_V,$$

where $\bar{r}_V$ = the radius of the bubble having average volume, then

$$\bar{r}_V = \sqrt[3]{[r]_3} \tag{37}$$

From the foregoing it appears that expressions giving several moments of the distribution of the true bubble radii in terms of one (preferably the 1st) or more moments of the distribution of the measured chord intercepts should provide a basis for calculating the desired quantities

DERIVATION OF AN EXPRESSION RELATING THE ACTUAL BUBBLE RADII TO THE MEASURED CHORD INTERCEPTS

In the following derivation,[3] it is assumed that the "linear traverse" method is performed by penetrating a representative volume of the sample with a random traverse line. It can be shown that this is analogous to the dual operation, actually carried out, of exposing a random section and running a random traverse line in the plane of the section. It is further assumed that sufficient length of traverse line is used so that·

(a) the effect of aggregate on the bubble distribution is averaged out, and
(b) the distribution of bubble sizes encountered in the traverse is representative of the distribution for the entire sample.

[3] The writer wishes to acknowledge the valuable help rendered on this phase of the discussion by G. W Lord and L. T Murray of the Research Division The former assisted in formulating the probabilities involved, while the latter solved the integral equation (44) and checked all the mathematics.

Let M = the total number of bubbles in a unit cube of concrete, and $F(u)\,du$ the proportion[4] having diameter u to $u + du$, where $\int_0^U F(u)\,du = 1$. (U being the diameter of the largest bubble.) Then the actual number of bubbles of diameter u to $u + du$ in the unit cube is

$$MF(u)\,du. \qquad (38)$$

Inject a line, perpendicular to the face of the cube, into the cube If there were only one bubble of diameter u_1 in the cube, the probability of penetrating that bubble with the line would be the ratio of the maximum sectional area of the bubble to the face area of the cube, i.e , if a statistically large number of lines was injected into the cube, the ratio of the number of lines penetrating the bubble to the total number of lines injected would not differ materially from the ratio of the maximum section area of the bubble to the face area of the cube This probability of penetration is then

$$\frac{\frac{\pi u_1^2}{4}}{1} = \frac{\pi u_1^2}{4}$$

If there are n_1 bubbles of diameter u_1 in the cube, the number of bubbles penetrated by the line is

$$\frac{\pi}{4} n_1 u_1^2 \qquad (39)$$

Now, if u_1 is the magnitude of u under consideration, i e. between u and $u + du$, from Eq. (38)

$$n_1 = MF(u)\,du.$$

Then, substituting in Eq. (39), the number of bubbles of diameter u to $u + du$ intersected by the line, per unit length of line is

$$\frac{\pi}{4} u^2 MF(u)\,du \qquad (40)$$

Extending the reasoning by which Eq. (39) was developed, if there are other bubble sizes present, say u_1, u_2, u_3, etc., the total number of bubbles of all sizes intersected by the line is

$$\frac{\pi}{4}\left(n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + \cdots n_Uu_U^2\right);$$

but the portion of the above expression in parenthesis divided by M is the second moment of u, which will be designated as $[u]_2$. Then the total number of bubbles of all sizes intersected by the line is

$$\frac{\pi}{4} M[u]_2 \qquad (41)$$

per unit length of line

Of all the bubbles penetrated by a uni length of the line, let $f(u)\,du$ be the pro portion which have diameters of u to $u + du$. Then the actual number of bubbles of this size penetrated by the line is

$$\frac{\pi}{4} M[u]_2 f(u)\,du.$$

But this number is also given by Eq. (40, above. Hence

$$\frac{\pi}{4} M[u]_2 f(u)\,du = \frac{\pi}{4} u^2 MF(u)\,du$$

and

$$f(u)\,du = \frac{u^2}{[u]_2} F(u)\,du. \qquad (42)$$

In one of the spheres of diameter u to $u + du$, picture a plane so situated that it is perpendicular to the penetrating line and contains the center of the sphere. It is obvious from Figure A that the sphere center lies at a distance y to $y + dy$ from the line; and also that the probability that a sphere of diameter u to $u + du$ has its center at a distance y to $y + dy$ from a random penetrating line is the ratio of the elemental area dA to the total plane area A, or

$$\frac{dA}{A}.$$

From the geometry of Figure A,

$$dA = 2\pi y\,dy, \quad A = \frac{\pi u^2}{4};$$

$$\text{and hence} \quad \frac{dA}{A} = \frac{8y\,dy}{u^2}.$$

[4] Synonomous with "the relative frequency".

It is also apparent that if a bubble is penetrated by the line so that the bubble center is at a distance y to $y + dy$ from the line, the length of line intercepted by the bubble is l to $l + dl$.

Again from Figure A,

$$y = \frac{\sqrt{u^2 - l^2}}{2}.$$

Then

$$dy = \frac{l\,dl}{2\sqrt{u^2 - l^2}},$$

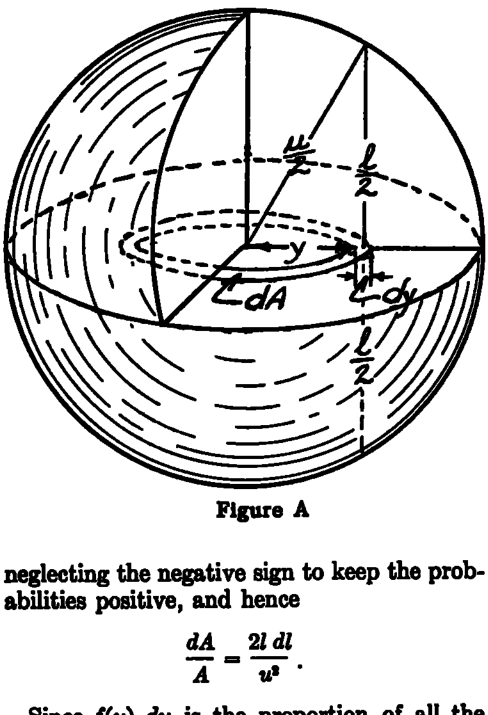

Figure A

neglecting the negative sign to keep the probabilities positive, and hence

$$\frac{dA}{A} = \frac{2l\,dl}{u^2}.$$

Since $f(u)\,du$ is the proportion of all the bubbles penetrated by the line, having a diameter u to $u + du$; and $\frac{2l\,dl}{u^2}$ is the probability that bubbles of this size, if penetrated, are penetrated so that the length of chord intercept is between l to $l + dl$, then the proportion of chord intercepts of length l to $l + dl$ resulting from penetration of bubbles of diameter u to $u + du$ is

$$\frac{2l\,dl}{u^2} f(u)\,du,$$

and from Eq. (42) is also given by

$$\frac{2l\,dl}{[u]_2} F(u)\,du$$

There being a distribution of bubble sizes, u may have any value greater than l up to some maximum value U. Hence, the proportion of chord intercepts having a length l to $l + dl$, resulting from penetration of all bubble sizes, is given by

$$\frac{2l\,dl}{[u]_2} \int_l^U F(u)\,du.$$

Denoting this proportion by $\phi(l)\,dl$,

$$\phi(l)\,dl = \frac{2l\,dl}{[u]_2} \int_l^U F(u)\,du,$$

and

$$\phi(l) = \frac{2l}{[u]_2} \int_l^U F(u)\,du. \tag{43}$$

From the two preceding equations, $\phi(l)$ is obviously the relative frequency function of the distribution of measured chord intercepts.

The quantity $[l]_i$; being the *ith* moment of the chord intercepts, is given by

$$[l]_i = \frac{n_1}{M} l_1^i + \frac{n_2}{M} l^i + \cdots \frac{n_s}{M} l_s^i.$$

Since $\phi(l)$ is the relative frequency function of l,

$$\frac{n_1}{M} = \phi(l_1)\,dl; \qquad \frac{n_2}{M} = \phi(l_2)\,dl,$$

etc.
then

$$[l]_i = l_1^i\phi(l_1)\,dl + l_2^i\phi(l_2)\,dl + \cdots l_s^i\phi(l_s)\,dl$$

$$= \int l^i\phi(l)\,dl,$$

and since l can have any value from 0 to U

$$[l]_i = \int_0^U l^i\phi(l)\,dl.$$

From Eq. (43)

$$[l]_i = \frac{2}{[u]_2} \int_0^U l^{(i+1)}\,dl \int_l^U F(u)\,du$$

On changing the order of integration, this reduces to

$$[l]_i = \frac{2}{[u]_2} \int_0^U F(u)\, du \int_0^u l^{(i+1)}\, dl. \quad (44)$$

Let

$$Q_i = \int_0^u l^{(i+1)}\, dl.$$

Integrating,

$$Q_i = \frac{u^{(i+2)}}{(i+2)}.$$

Substituting in Eq. (44),

$$[l]_i = \frac{2}{(i+2)[u]_2} \int_0^U u^{(i+2)} F(u)\, du.$$

Now the quantity $[u]_i$ is the *ith* moment of the distribution of actual sphere diameters, and from a derivation similar to that for $[l]_i$ above,

$$[u]_i = \int_0^U u^i F(u)\, du.$$

Hence,

$$[l]_i = \frac{2[u]_{(i+2)}}{(i+2)[u]_2}. \quad (45)$$

This equation is valid for all values of $i \gtreqless -1$. Solving it for various values of i

$$[l]_0 = \frac{2[u]_2}{2[u]_2} = 1, \text{ as it should be,}$$

$$[l]_1 = \frac{2[u]_3}{3[u]_2}, \quad (46) \qquad [l]_2 = \frac{[u]_4}{2[u]_2}, \quad (47)$$

$$[l]_{-1} = \frac{2[u]_1}{[u]_2}; \quad (48)$$

but

$$[l]_{-1} = \frac{1}{l_{(hm)}}$$

where $l_{(hm)}$ = the harmonic mean of the chord intercepts, and hence

$$l_{(hm)} = \frac{[u]_2}{2[u]_1}.$$

Other moments can be obtained by solving Eq. (45) for higher values of i

To convert the moments of the distribution of bubble diameters to the moments of the radii:

$$[u]_1 = 2[r]_1, \quad (49) \qquad [u]_3 = 8[r]_3, \quad (51)$$

$$[u]_2 = 4[r]_2, \quad (50) \qquad [u]_4 = 16[r]_4. \quad (52)$$

Then, from Eq. (46), and (49),

$$[l]_1 = \frac{4[r]_3}{3[r]_2} \quad (53)$$

and from Eq (47) and (50),

$$[l]_2 = \frac{2[r]_4}{[r]_2} \quad (54)$$

etc.

EQUATIONS FOR DETERMINING THE AIR CONTENT AND THE SPECIFIC SURFACE OF THE AIR BY THE CHORD INTERCEPT MEASUREMENTS

The equation for the volume of air per unit volume of concrete is derived as follows:

Since by Eq. (37) $\bar{r}_v$, the radius of the bubble of average volume is equal to $\sqrt[3]{[r]_3}$, the volume of air per unit volume of concrete is given by

$$A = \frac{4\pi M[r]_3}{3} \quad (55)$$

where M = the true number of bubbles per unit volume of concrete; and from Eqs. (41) and (50)

$$n = \frac{\pi M[u]_2}{4} = \pi M[r]_2, \quad (56)$$

where n = the number of bubbles intersected per unit length of traverse. Dividing Eq. (55) by Eq. (56)

$$\frac{A}{n} = \frac{4[r]_3}{3[r]_2}$$

From Eq. (53), and the fact that $\bar{l} = [l]_1$ by method of calculation,

$$\bar{l} = \frac{4[r]_3}{3[r]_2} \quad (57)$$

Hence

$$\frac{A}{n} = \bar{l},$$

and

$$A = n\bar{l}, \quad (18)$$

which is Mr. Powers' Eq. (18).

Following is the derivation of the equation for the specific surface of the air bubbles, i.e. the bubble surface area per unit volume of air:

The total surface of the bubbles in a unit volume of concrete is given by

$$S_T = 4\pi M[r]_2, \qquad (58)$$

and the total volume of air by

$$V_T = \frac{4\pi}{3} M[r]_3, \qquad (59)$$

Then, the specific surface being designated as

$$\alpha = \frac{S_T}{V_T} = \frac{3[r]_2}{[r]_3}$$

But from Eq (57)

$$\frac{[r]_3}{[r]_2} = \frac{3\bar{l}}{4}$$

Hence

$$\alpha = \frac{4}{\bar{l}} \qquad (19)$$

From the foregoing, it is obvious that the equations for air content and specific surface, as given by Mr. Powers, are applicable to any system of spherical dispersoids whether the system is made up of single or multi-sized spheres.

THE PHYSICAL SIGNIFICANCE OF $\bar{r}_h$

Mr. Powers' Eq. (22) states

$$\bar{r}_h = \tfrac{3}{4}\bar{l} \qquad (22)$$

where $\bar{l}$ = the arithmetic mean (or first moment) of the measured chord intercepts, as a result of the method of calculation, and

$\bar{r}_h$, originally defined as the radius of the bubble having average volume, is now the radius of bubbles in a hypothetical system of bubbles of uniform size

Study of Eqs (37), (46), (50), and (51) makes it obvious that if Mr. Powers' Eq (22) is correct, $\bar{r}_h$ cannot be the radius of the bubble of average volume It can be shown that if a system of bubbles of uniform size is penetrated by a random line, and if $\bar{l}$ is the arithmetic mean of the chords intercepted, Eq 22 gives the radius of the bubbles From this fact it might be assumed that such was its source. However, air entrained in concrete is not made up of uni-size bubbles but consists of a distribution of sizes covering an appreciable range. For the latter system, Equation (22) does not give any of the mean radii defined in Eq. (33), (35), or (37); since in the system of bubbles of uniform size, the relative probability of penetrating bubbles of different sizes is not a factor, whereas in the latter system it must be taken into account.

Despite the fact that $\bar{r}_h$ does not represent any of the mean radii of a system of distributed bubble sizes, it does have some physical significance for such a system.

Eq (53) shows that for a system containing a distribution of bubble sizes, which system is pierced by a random line, the first moment of the chords intercepted by the bubbles on the line, is given by

$$[l]_1 = \frac{4[r]_3}{3[r]_2}. \qquad (53)$$

By the method of calculation, Powers, $\bar{l}$ is the arithmetic mean or first moment of the observed chord intercepts Then $[l]_1 = \bar{l}$, and from Eq. (53)

$$\bar{l} = \frac{4[r]_3}{3[r]_2} \qquad (60)$$

and hence

$$\frac{[r]_3}{[r]_2} = \frac{3\bar{l}}{4} \qquad (61)$$

and from Eq. (22) and (61)

$$\bar{r}_h = \frac{[r]_3}{[r]_2} \qquad (62)$$

Since $\bar{r}_h$ is by Eq (22) equal to $\frac{3\bar{l}}{4}$, and since, as stated above, $\frac{3\bar{l}}{4}$ would give the radius of bubbles in a system of uniform sized bubbles analysed by the chord intercept method, $\bar{r}_h$ must be the radius of bubbles in such a system To determine what significance $\bar{r}_h$ has for a system of bubbles of distributed sizes, let us compare properties of the two systems. In the system of bubbles of distributed sizes, let

V_D = the volume of air per unit volume of concrete,

S_D = the surface area of air per unit volume of concrete, and

M = the number of bubbles per unit volume of concrete.

In the system of uniform sized bubbles, let

V_U = the volume of air per unit volume of concrete, and

S_U = the surface area of air per unit volume of concrete,

N = the number of bubbles per unit volume of concrete.

For the bubble system having distributed sizes, from Eq. (36)

$$V_D = \frac{4\pi}{3} M[r]_3, \tag{63}$$

and from Eq. (34)

$$S_D = 4\pi M[r]_2. \tag{64}$$

For the system of uniform sized bubbles,

TABLE A

Spec No	Air Content		n Per cm	α cm.⁻¹	No Bubbles per cu cm		Mean Radius × 10³ cm		Paste percent, $p \times 10^2$	Spacing Factor × 10 cu cm Based on		
	Air Meter	Microscope			N	M	$\bar{r}_h$	$\bar{r}_A$		$p/4n$	$N\bar{r}_h$	$M\bar{r}_A$
	%	%										
CAA2	1 49	1 90	960	159	864	6,770	18 85	4 49	26 3	68 6	41 6	25 5
CAC3	4 65	4 09	3 515	334	13,950	48,200	8 96	3 91	25 1	17 9	15 0	11 9
CAD1	5 39	5 35	2 732	198	3,790	26,870	15 14	4 73	23 9	21 9	21 7	14 5

$$V_U = \frac{4\pi}{3} N\bar{r}_h^3, \tag{65}$$

and

$$S_U = 4\pi N\bar{r}_h^2 \tag{66}$$

In order for $\bar{r}_h$ to have any significance for the bubble system of distributed sizes, $\bar{r}_h$ and N must be selected so that the volumes of air per unit volume of concrete are identical in each system, i e ,

$$V_U = V_D$$

It follows from Eq (63) and (65) that

$$\frac{4\pi}{3} N\bar{r}_h^3 = \frac{4\pi}{3} M[r]_3$$

and

$$N = \frac{M[r]_3}{\bar{r}_h^3} \tag{67}$$

Substituting the above value of N and the value of $\bar{r}_h$ from Eq. (62) into Eq. (66),

$$S_U = 4\pi M[r]_2,$$

which value is identical with that for S_D obtained in Eq. (64). In other words, the surface areas of the two systems are the same; and since the two systems were set up to have the same volume of air per unit volume of concrete, it follows that the specific surface of the air in the two systems is the same

Therefore $\bar{r}_h$ is the radius of the bubbles of a system of uniform sized bubbles having the same volume of air per unit volume of concrete and the same specific surface of air bubbles as the system of random sized bubbles for which $\bar{l}$ is measured.

THE RELATIONSHIP OF N TO THE ACTUAL NUMBER OF BUBBLES

As pointed out by Mr. Powers, N is not the actual number of bubbles per unit volume of concrete. Consideration of Eqs. (62) and (67) will demonstrate this and also that the relationship between the two magnitudes is not constant. By another method of microscopic analysis, called an areal traverse,[5] it is possible to obtain the actual number of bubbles For the few samples thus far examined by both methods, the true number was from 3½ to 8 times the value of 'N'. (See Table A)

LIMITATIONS OF THE CHORD INTERCEPT METHOD

Examination of equations (46) through (54) reveals that it is not possible to express any single moment of the true radii in terms of moments of the chords only. Thus it is not possible to express $\bar{r}_A$, $\bar{r}_s$, $\bar{r}_v$, or M in terms of moments of the chords These factors can be expressed in terms of moments of the section diameters, which can be obtained from an areal traverse.[5] However, performance of

[5] A description of the Areal Traverse Method, together with the mathematical derivation of the necessary equations, is on file at the Highway Research Board or can be obtained from the author of this discussion.

an areal traverse is a very tedious operation when the air content is over 3 percent. Pending establishment of the necessity for determining these factors it will never be widely used.

THE BUBBLE SPACING FACTOR

In Part 1 of the paper, Mr. Powers shows that for a specific paste having a saturation coefficient greater than 91 percent and undergoing cooling at a certain rate, L_{max} gives the theoretical maximum distance from any point in the paste to an air-paste interface which can occur without disruptive hydraulic pressure being generated. The spacing factor, used to characterize the bubble system of a specific sample of concrete, should be a magnitude which can be compared with the calculated L_{max}. Obviously, with a random distribution of bubble centers and a range of bubble sizes, the bubble spacing will vary from point to point in the paste. Since L_{max} is a measure of a maximum distance, it would seem that the maximum bubble spacing occurring in actual concrete would have to be determined before a decision could be made on whether the concrete might be subjected to critical pressure. On the other hand if there were only a few occurrences of the maximum spacing in a considerable volume of paste, (and this maximum approximated the calculated critical distance) it would seem doubtful that sufficient stress would be engendered to cause failure of the specimen.

To illustrate, suppose it were possible to measure all distances from bubble to bubble in a representative volume of paste. A plot of these measurements against number of occurrences would probably give a typical distribution curve such as shown in Figure B. Suppose the ordinate of M, (the maximum spacing) represented an occurrence of only 1. If the calculated critical spacing approximated the abscissa of M, it is doubtful that the specimen would fail. On the other hand, if the calculated critical spacing were smaller than M, say C, the number of actual occurrences of such spacing would be larger, and the probability of failure greater If C should be as small as A, the arithmetic mean of all the spacings, some 50 percent of the spacings would exceed the critical and failure would certainly occur. It therefore appears that the factor used to characterize the bubble system of a concrete specimen should be a magnitude greater than the arithmetic mean but smaller than the maximum spacing.

Mr. Powers gives two approximations of such a factor. The first is simply the ratio of the volume of unaerated paste to the total surface area of the air-paste interface. In this form the spacing factor is obviously an average thickness of the paste envelopes surrounding the air bubbles.

The other factor is given by Eq. 24, applied to a hypothetical bubble system. The assumption is made that the aerated paste volume is divided into continuous cubes of equal size, and that each cube contains one (and only one) air bubble so placed that the bubble and cube centers coincide. The bubbles are assumed to be of uniform size and the size and

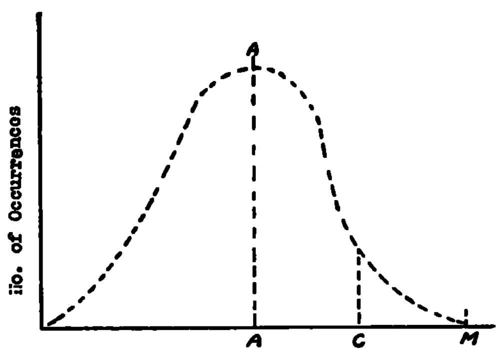

Figure B

number chosen so that the hypothetical system has the same total volume and surface area of bubbles as the actual system. If the air-bubbles in concrete were of a single size and $\bar{r}_h$ were the true radius, Eq. (24) would give the average spacing for the system. However, for an actual specimen of aerated concrete, the first assumption is not valid and hence the second cannot be correct. The hypothetical system used in deriving the spacing factor has two characteristics, volume and specific surface of air bubbles, that are identical with the actual system However, the two systems differ radically in a third characteristic, i.e., the number of bubbles. Just what significance such a spacing factor has for a random sized bubble system is not clear to the writer.

Another spacing factor derived in this laboratory, based on Mr. Powers' Eq 24 but calculated from the actual number of bubbles and the arithmetic mean radius, gives a mean of the distances from cube corner to bubble boundary for all bubbles in the system. This factor, except for the limitations on the distribution of bubble centers imposed in the derivation, would be represented by the abscissa of point A in Figure B. It is probably a fair approximation of the mean spacing of an actual bubble system.

In Table A, values of all three factors are given for three specimens tested in this laboratory. The specimens were identical as to aggregates, cement, and W/C; the first contained no aerating agent while each of the other two contained a different agent. It is apparent from the results shown that both of Mr. Powers' factors are larger than the mean factor. From the reasoning outlined above, this deviation from the mean seems to be in the right direction, but it remains to be proven that the magnitude of either factor approximates the desired quantity.

To summarize—in the writer's opinion none of these factors has been proven to give an exact measure of the desired quantity; the mean spacing factor is too small, either of Powers' factors (for the few specimens tested) gives values larger than the mean but it is not known that the magnitudes are correct; however, in view of the fact that the derivation of the equations for L_{max} is not rigorous, either of Mr. Powers' factors should serve qualitatively until such time as a more refined factor is needed or forthcoming.

SYMBOLS

Symbols similar to those used by Mr. Powers have the same significance he assigned them. Symbols introduced in the Discussion are defined as follows:

$f(u)$ = an unknown function of u; the relative frequency function of actual bubble diameters for those bubbles intersected by the traverse line.

$F(u)$ = an unknown function of u; actually the relative frequency function of the true diameters of bubbles in a system containing distributed sizes.

$\phi(l)$ = an unknown function of l; the relative frequency function of the measured intercepts.

l = the length of traverse line intercepted by a bubble.

$[l]_i$ = the ith moment of the measured chord intercepts, where i is any integer.

$l_{(hm)}$ = the harmonic mean of the measured chord intercepts.

M = the true number of bubbles per unit volume of concrete.

$[m]_i$ = the ith moment of a series of magnitudes, m_1, m_2, m_3, etc., where i is any integer.

n = the number of bubbles, per unit length of traverse, intersected by a traverse line.

$[r]_i$ = the ith moment of the true bubble radii in a system containing bubbles of various sizes.

$\bar{r}_A$ = the arithmetic mean radius of a system of bubbles of various sizes.

$\bar{r}_s$ = the radius of the bubble having average surface area, in a system containing bubbles of various sizes.

$\bar{r}_v$ = the radius of the bubble having average volume, in a system of bubbles of various sizes.

u = the true diameter of an air bubble.

$[u]_i$ = the ith moment of the true bubble diameters.

U = the true diameter of the maximum sized bubble in a system containing various sizes.