REVIEW OF LITERATURE ON AIR-ENTRAINED CONCRETE

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Air Entrainment in Concrete

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TABLE OF CONTENTS

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LIST OF FIGURES

LIST OF TABLES

Review of Literature on Air-Entrained Concrete

Introduction

This report results from preparation for research concerned with the entrained air system in concrete, and should provide a comprehensive review of the present state of knowledge in this area. The material is organized to answer the following basic questions in the order presented.

1. How was air entrainment discovered?
2. What parameters define an entrained air system?
3. How is air entrained in concrete?
4. What properties does entrained air contribute to the concrete?
5. What factors are presently known to affect the properties of the entrained air system?
6. What new technology is needed to promote the achievement of desirable entrained air systems?

1. Discovery of Air Entrainment

The history of air entrainment in concrete may be traced to the early 1930's at which time it was determined that,

> ". . . portland cement that inadvertently contained 'crusher oil' reduced surface scaling as did many of the blends of portland and natural cement that contained tallow added during grinding of the natural cement. Laboratory tests disclosed that the beneficial effect of the crusher oil and tallow was due entirely to the additional air entrapped in the concrete by these air-entraining agents." (1)

The discovery of this phenomenon was quite by accident as pointed out by Jackson. Introducing the subject of "Concrete Containing Air Entraining Agents," Jackson (2) states,

> "... I should like to trace briefly the development of the idea of introducing air into concrete for the purpose of improving durability. As we all know, the practice of applying sodium or calcium chloride, either mixed with sand and cinders or in the raw state, to icy pavements tends to induce surface scaling, particularly on new concrete. In an attempt to prevent this trouble the New York State Highway Department several years ago introduced the practice of blending natural with portland cement in its pavement concrete using a proportion of about 15 percent natural to 85 percent portland. Preliminary field experiments indicated that concrete containing the blended cement was considerably more resistant to salt action than comparable concrete made entirely of portland cement. In fact, the results were so outstanding that New York State, as well as most of the New England States, adopted the use of the blend as standard practice.
>
> "Speculation as to the reasons for this superior resistance developed two schools of thought. On the one hand it was argued that the improvement was due to certain desirable characteristics inherent in the natural cement itself. On the other hand, the fact that, of the two natural cements used in New York State, the one which had produced the best results contained a small amount of beef tallow used as a grinding aid led many to wonder whether the improvement in scale resistance was not due merely to this fact or, in other words, whether the same benefits would not be derived by intergrinding the tallow with the portland cement itself. Incidentally, this view was strengthened considerably by the discovery about this time that a certain portland cement having an exceptionally good service record in New York State contained a small quantity of oil or grease which had contaminated the cement as the result of leakage from the crusher bearings.
>
> "Recognizing the seriousness of the scaling problem, the Portland Cement Association about this time began an intensive study of air-entraining agents. The effect of introducing small quantities of materials such as tallow, fish oil stearate, resin, etc., either interground with the cement or introduced in liquid form at the mixer, was studied both in the laboratory and in the field.
>
> "Beginning in 1938 a number of experimental concrete pavements were constructed by several of the State Highway departments, certain cities and others, with the idea of demonstrating the effectiveness of this treatment under field conditions. The several test roads built by New York State, and the experimental street work carried out by the City of Minneapolis are examples. However, the field demonstration which has probably been most striking and certainly the best known is the one conducted by Moore at the Hudson plant of Universal-Atlas. These tests, with which you are all familiar, indicated definitely the possibilities of utilizing the air-entraining characteristic of certain materials to improve durability."

Thus, the practice of intentionally entraining air bubbles in concrete was introduced in the 1930's and it has since become one of the most important developments in concrete technology. As pointed out, the main purpose of introducing air into concrete is to protect it from the potentially destructive effect of freezing and thawing. Air may also be introduced to aid in the workability of concrete having a low cement content.

2. Parameters Defining the Entrained Air System

In order to investigate the air void system in hardened concrete, a surface must be prepared by sawing and polishing the concrete to expose the air bubble sections. This prepared surface is observed through a linearly traversing microscope and the bubble sections intersected by the traverse line are counted and the length of the bubble chords measured. With information thus obtained, various parameters may be determined.

ASTM designation C457-60T (3) applied the following definitions and symbols to the parameters of the air void system:

> "(a) Air Void—A small space enclosed by the cement paste and concrete and occupied by air. This term does not refer to capillary or other openings of submicroscopical dimensions or to voids within particles of aggregate. Air voids are almost invariably larger than $2\ \mu$ in diameter. The term includes both 'entrapped' and 'entrained' air voids . . .
>
> "(e) Air Content, A—The proportional volume of air voids in concrete expressed as a percentage of the volume of the hardened concrete.
>
> "(f) Paste Content, P—The proportional volume of cement paste in concrete, expressed as a percentage of the volume of the hardened concrete, calculated as the simple summation of the proportional volumes of the cement and water included in the concrete mixture.
>
> "(g) Specific Surface, α—The surface area of the air voids in hardened concrete, expressed as square inches per cubic inch of air void volume.
>
> "(h) Chord Intercept, $\bar{l}$—The average length of chord across the cross-sections of the air voids intercepted by a line of microscopical traverse, in inches.
>
> "(i) Number of Air Voids Per Inch of Traverse, n—The number of air voids intercepted by a line of microscopical traverse, in number of air voids per inch of traverse."

Powers Spacing Factor, $\bar{L}$—The Powers spacing factor is an index related to the maximum distance of any point in the cement paste from the periphery of an air void, in inches. The calculation of the spacing factor of the air-void system is based upon an assumption that all air voids in the sample are equal-sized spheres arranged in a simple cubic lattice throughout the cement paste. Figure 1, diagram A, shows a single cube of the lattice with an air void centered in the cube. The Powers spacing factor, $\bar{L}$, is shown geometrically to be one-half the diagonal length of the cube minus the radius of the air void.

Philleo Factor, S—According to Larson, et al. (4), this factor defines,

> ". . . the distance which, in a given percentage of cases, is equal to or greater than the distance from any given point in the paste to the nearest air bubble.
>
> ". . . it may be thought of as the thickness of spherical shells concentric with randomly distributed air voids such that the volume contained within all such spheres in a unit volume of paste constitutes a given percentage of the paste."

The Philleo Factor is shown in Figure 1, diagram B.

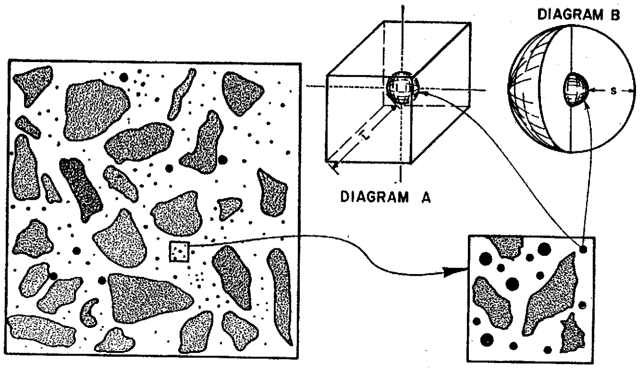

Figure 1. Polished section of air-entrained concrete as seen through a microscope.

3. Entrainment of Air in Concrete

During the mixing of concrete, layers of air are trapped between the in-folding surfaces of paste. These layers are quickly broken up and dispersed as bubbles, which in the presence of agitation collide and tend to coalesce. Coalescence is a natural tendency for air bubbles because it is accompanied by a reduction of interfacial area and pressure within the bubbles; thus a reduction in the energy of the system results.

Coalescence is accompanied by an increased probability that the bubbles will escape during mixing because it creates large bubbles possessing higher buoyant forces. For escape to occur during mixing, the bubble near the surface must exert enough buoyant force to move through the paste at a rate that will enable it to reach the surface before circulation removes it from the surface region.

A principal function of the air-entraining agent is to prevent this coalescence by forming a film at the interface of the bubbles. This film is more effective when it prevents migration of air from small to large bubbles and causes adhesion of minute bubbles to solid particles in the concrete. The film must also resist deterioration with time and be elastic enough to sustain short time loads.

There are many agents capable of entraining air in concrete. In an extensive evaluation program conducted by the Bureau of Public Roads (5) 27 commercial admixtures submitted for test were classified in the following seven categories:

(1) salts of wood resins (pine wood stumps),
(2) synthetic detergents (petroleum fractions),
(3) salts of sulfonated lignin (paper pulp industry),

(4) salts of petroleum acids (petroleum refining),

(5) salts of proteinaceous materials (processing of animal hides),

(6) fatty and resinous acids and their salts (paper pulp and animal hide processing), and

(7) organic salts of sulfonated hydrocarbons (petroleum refining).

Entrained air is present in concrete in voids of two general types. As stated by Mielenz et al. (6), these types are, "(1) those subjected only to capillary and hydraulic pressure of water in the fresh concrete; and (2) those called 'entrapped' voids and 'entrained' air bubbles, respectively. The 'entrapped' voids are ineffective or harmful in unhardened concrete because they do not increase the spacing of solid particles in the mass and hence they do not decrease the dilatancy necessary to manipulation. Entrained air bubbles increase the spacing of the solid particles and decrease the dilatancy; moreover, they facilitate movement of particles of aggregate by separating solid surfaces and sustaining short-time loads."

4. Properties Contributed to Concrete by Air Entrainment

From the advent of air-entrained concrete in the 1930's until 1945, little was known of the mechanism through which air entrainment increased frost resistance. Using experimentally determined properties, Powers (7) obtained information in 1945 which contributed significantly to the understanding of frost action in concrete.

Powers found that not only is the total volume of air contained in the concrete important, but more so is the size and spacing of the air voids comprising the total volume. These findings were arrived at through an investigation of the hydraulic pressure developed within the concrete paste during freezing.

As stated by Powers,

> "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.
>
> "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."

Thus, Powers introduced a factor defined as the maximum average distance from a point in the paste to the nearest air void and indicative of the distance water would have to travel during the freezing process in order to reach an air void. According to Powers, if these voids were spaced closely enough together, the internal hydraulic pressure created by the resistance to flow of excess water would be sufficiently low to prevent rupture of the paste in tension. Analysis of laboratory freeze-thaw data available at that time led Powers to propose that the magnitude of this distance be equal to or less than .01 inches.

More recent work by Mielenz et al. (8) indicates an upper limit of about .008 inches. Figure 2 shows the correlation between Powers spacing factor and freezing and thawing resistance. The results of previous findings are shown by the dashed line in Figure 2.

Extensive freezing and thawing tests by Klieger (9) provided further substantiation of the void spacing concept.

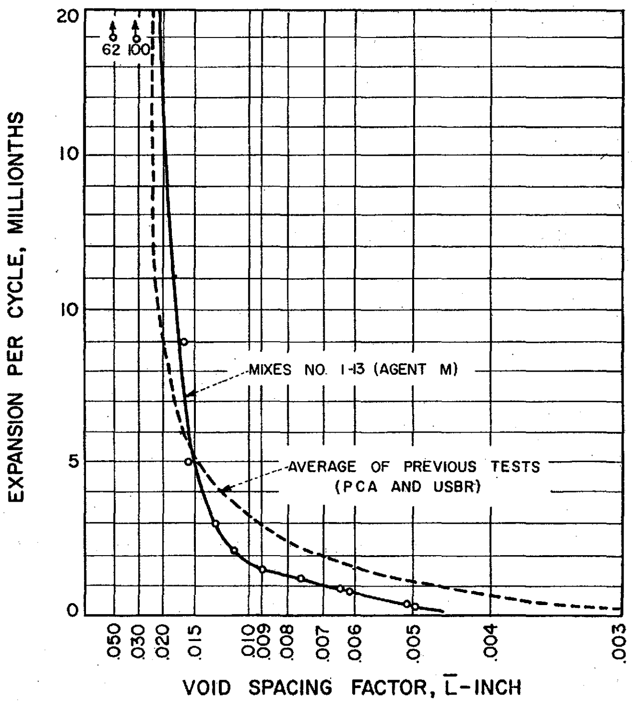

Figure 2. Correlation of void spacing factor and freezing and thawing expansion; amount of agent varied (figure taken from Reference 8).

Another approach to the void spacing concept has been under investigation recently by Larson (4) et al. They state:

> "Research by Powers advanced the concept of hydraulic pressure as the principal destructive mechanism and the role of entrained air bubbles in reducing such pressure to tolerable levels. Brown and Pierson applied the Rosiwal traverse method to the problem of measuring the parameters of the void system which Powers had conceived as being most significant. These were air content, bubble chords per unit length of traverse, specific surface, and spacing factor. Spacing factor has been considered the best indicator of the adequacy of an air-void system, but limits for this parameter, which will assure good correlations with performance, are not logically determinable. Total air content, perhaps the most widely used parameter, often fails to be a reliable indicator of frost resistance because it does not reflect the quality of an air void system."

The parameters chosen by Larson et al. were evaluated by a laboratory test program in which test specimens were subjected to Powers test cycle to determine frost susceptibility. They report that (4), ". . . Specimen dilations correlated with increasing cycle numbers in all cases and most probable tenth cycle dilation was determined for each specimen." Of the parameters investigated, they state that, "a factor indicating the protected paste volume, termed the Philleo spacing factor, was found to give the best correlation."

This parameter was suggested by R. E. Philleo (10) in 1955, and according to Philleo, is the distance equal to or greater than the distance from any given point in the paste to the nearest air bubble for a given percentage of cases.

For the data reported by Larson et al., Powers spacing factor ranged from a low value of .00678 inches to a maximum value of .01568 inches while the Philleo spacing factor ranged between the values of .002812 and .008568 inches, respectively.

In summary, the principal purpose of entraining air in concrete is to protect the paste from the potentially destructive forces generated during the freezing process. This protection is derived from the cellular paste structure produced by the randomly dispersed air bubbles and is related to the thickness of the cellular walls. Both the Philleo and Powers factors are to some extent approximations of the average wall thickness and are dependent upon the frequency of air voids and their size distributions. Therefore, a change in the frequency and size distribution of air voids and concomitantly the Powers and Philleo factors affects the freeze-thaw resistance of air entrained concrete.

Aside from the Powers and Philleo factors, some commonly used parameters for defining the frequency and void size distribution are specific surface area of the voids, total number of voids per unit volume of paste or concrete and mean void diameters.

The theoretical basis for these parameters and the mathematical relationships between them are given by Lord and Willis (11).

Equations relating the above parameters to the Philleo and Powers spacing factors are presented in reference (4) and (11), respectively.

5. Factors Affecting the Properties of the Entrained Air Void System

In an unhardened, air-entrained concrete, numerous factors significantly influence the size distribution and frequency of the air void system and therefore, the frost resistance of the hardened concrete.

Results of numerous investigations have shown that the following factors significantly influence the void size distribution and frequency:

(1) Properties of the air-entraining agent.

(2) Water-cement ratio.

(3) Properties of the solids in the concrete mixture.

(4) Manipulation and consolidation of the concrete.

The influence of these factors on the air void system may be investigated by observing changes in the determination parameters of the void system (i.e., spacing factors, specific surface area, mean diameters, number of bubbles).

Properties of the Air-Entraining Agent

Air-entraining agents, when added to concrete, may behave in one of two ways. The agent may remain soluble and become adsorbed at the air-liquid interface or it may produce an insoluble precipitate which surrounds an air bubble when it is caught in the interface between the water and air.

Air-entraining agents which remain soluble and are positively adsorbed at the air-water interface are said to be surface active. Such materials cause a reduction in surface tension of the water. Mielenz et al. (6) have reported that a reduction of as much as 18 dynes per centimeter may be expected at concentrations of surface active agents normally used in practice. Glasstone (12) states that there are indications of ". . . the formation of unimolecular layers at the surface of a solution containing a substance producing a marked lowering of surface tension." He further states that ". . . there may be some tendency, in certain cases, for thicker layers to form to a limited extent." Thus, these agents may produce a "film" around air bubbles which has a thickness of only one molecule.

On the other hand, agents which produce insoluble precipitates form a "film" in the interfacial region described by Mielenz et al. (6) as ". . . a solid or gelatinous film . . . characterized by finite thickness, strength, elasticity, permeability, and other properties which, together, control the subsequent response of the air bubble to mechanical or physical-chemical changes in the system."

Mielenz et al. (6) found that those agents which produce insoluble products with calcium hydroxide and are not likely to function as surface active agents are:

(1) Sodium soap of wood resin.

(2) Sodium abietate.

(3) Sodium soaps of lignin derivatives, rosin, or fatty acid.

(4) Triethanolamine salts of sulfonic acids.

Many agents based on sulfonates do not form insoluble precipitates and are therefore likely to function as surface active agents in concrete.

The "film" so formed by air-entraining agents has been thought by some to be of importance because coalescence of bubbles and the rate of dissolution of the air in the bubbles may be reduced to an extent depending on various properties of the air-entraining agent. As stated by Mielenz,

> ". . . adsorbed films at air-water interfaces produced by satisfactory air entraining agents decrease the rate of transfer of air, decrease the tendency of bubbles to coalesce, permit bubbles to bear short-time loads, and decrease the work necessary to reproduce bubbles of given specific surface area."

To investigate the variability between agents in producing small bubbles and preventing coalescence and passage of air through the "film" of the agent, Mielenz generated air bubbles using various agents in the presence of portland cement slurry.

The results are shown in Figure 3. Agents F and L gave rise to comparably large bubbles which dissolved completely, in a short period of time. Agent C produced small bubbles (about 18 and 28 microns in diameter) which decreased in size until finally becoming stabilized at some smaller diameter. Three bubbles were observed using Agent J. These bubbles behaved in much the same manner as those produced by Agent C, but stabilization was achieved at a smaller diameter.

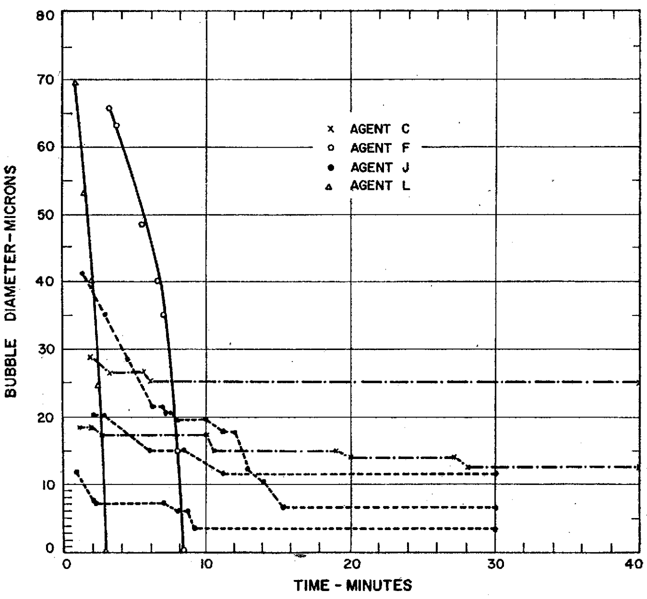

Figure 3. Relationship of bubble size to time in water solutions of four air-entraining admixtures in the presence of portland cement (1 g per 30 ml of solution)—Agents J and L, 3 drops in 30 ml distilled water; Agent F, 60 mg in 30 ml distilled water; Agent C, 1 drop in 30 ml distilled water; determinations at 24.5-29° C (figure taken from Reference 6).

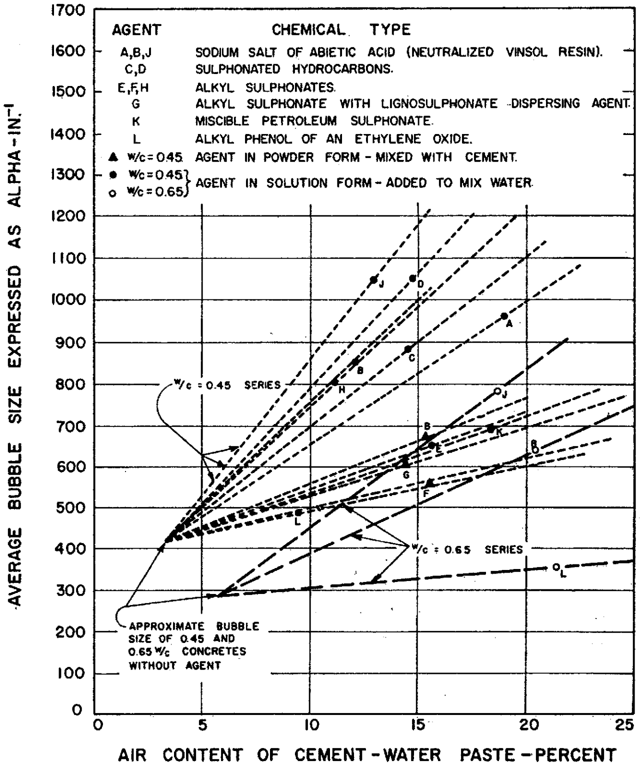

Figure 4. At the same air content in the paste, the average bubble size was influenced by the type and form of the agent and the amount of fines in the concrete, as expressed by the water-cement ratio (figure taken from reference 8).

There is a tendency for air to transfer from small to large bubbles if the mix water is saturated with air. When the mix water is not saturated with air there is a tendency for the air in small bubbles to go into solution because of the inherent higher pressure in these small bubbles due to surface tension.

If those processes occur to a significant extent during the setting period of concrete, they will increase the difficulty of producing hardened concrete containing high specific surface area bubbles for a given air content and thereby increase the difficulty of producing frost resistant concrete.

Bruere (13) has observed that in cement paste, a negligible amount of air is transferred from bubble to bubble as a result of the inability of the "film" to prevent the passage of air. He states that, "Negligible rearrangement of bubble sizes and solution of air from small bubbles occurred during the period that air-entrained cement pastes are fluid prior to setting," and that ". . . the type of bubble film appears to be an unimportant factor in the transference of gas between bubbles in cement pastes."

The relative effectiveness of various air-entraining agents in producing a system of air bubbles possessing high specific surface area is shown in Table I[1] and Figure 4.

The type and amount of air-entraining agent required to produce an air content of 5 percent as deter-

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[1] Tables may be found in the Appendix.

mined by the air meter were the principal variables. Agents A, B, C, D, and J were well known air-entraining agents meeting the specifications of ASTM C-260 at the time the research was conducted. Agent I was not a true air-entraining agent. Agent L was an air-entraining agent produced outside the United States.

Figure 4 shows that Agents A, B, C, D, J, and H (in liquid form) produced small bubbles while the use of Agents B, E, F, G, and L (in powder form) produced larger bubbles. The specific surface areas for the agents producing the small bubbles ranged from a high value of 1143 in^2/in^3 to a low of 800 in^2/in^3. Correspondingly, the specific surface areas for the group producing the larger bubbles were 678 in^2/in^3 to 476 in^2/in^3.

The divergence of the dashed lines in Figure 4 indicates that differences in specific surface area may be attribued to the agent used rather than the amount used. Bruere (14) also found this to be true.

From present knowledge, the following conclusions may be made concerning air-entraining agents:

1. No data have been presented which indicate that one class of agents is superior to the other. (Classes of agents being those agents that produce insoluble precipitates as opposed to the surface active agents.) Within classes, however, different agents may entrain bubbles with widely different specific surface areas.

2. Among the surface active agents, Lauer (15) and Bruere (14) reported the anionic type to be superior to the cationic type and the cationic to be superior to the nonionic type.

3. Mielenz et al. (6) report that derivatives of abietic acid and sulfonated hydrocarbons produce somewhat smaller voids than do other types of air-entraining agents.

4. The air-entraining agent and the amount used affect the size distribution and frequency of the air voids.

5. Negligible rearrangement of bubble sizes and solution of air from small bubbles occurs during the period that air-entrained cement pastes are fluid prior to setting.

6. The type of bubble film appears to be an unimportant factor in the transference of gas between bubbles in cement pastes.

The Effect of the Water-Cement Ratio

For a given concrete mixture, as the water-cement ratio increases, the air content increases and the specific surface area of the bubbles decreases.

This can be understood by considering the mechanisms through which air is introduced into the mixture. As pointed out by Powers (16) air presumably enters concrete as a result of the infolding action of the fluid mixture. As the fluid mixture becomes stiffer, the infolding action is confined to the vicinity of the mixing source while the remainder of the mixture is quiet. Thus, the stiffer the mix (lower the water-cement ratio) the less air entrained.

Lower specific surface area of the air void system due to increased water-cement ratio is a result of low shear stress in the more fluid material. Powers has pointed out that higher shear stresses exist in the more viscous materials (low water-cement ratio) enabling division of smaller bubbles than would otherwise occur. Conversely, a high water-cement ratio produces a more fluid material with low shear stresses unable to divide the larger bubbles. This results in a void system of low specific surface area.

Figure 5 illustrates the effect of the water-cement ratio on the air content and the specific surface area of the air void system. In one concrete mixture, the amount of air-entraining agent was held constant while in the other mixture the amount of agent was varied to give constant air content. A study of these curves indicates that an increase of water-cement ratio with the amount of air-entraining agent held constant tends to increase the size of the bubbles (decrease the magnitude of the specific surface) and to increase the air content of the cement paste greatly.

The relative size distribution and number of voids is also significantly affected by the water-cement ratio of the mixture. This is illustrated in Figure 6 and Table II.

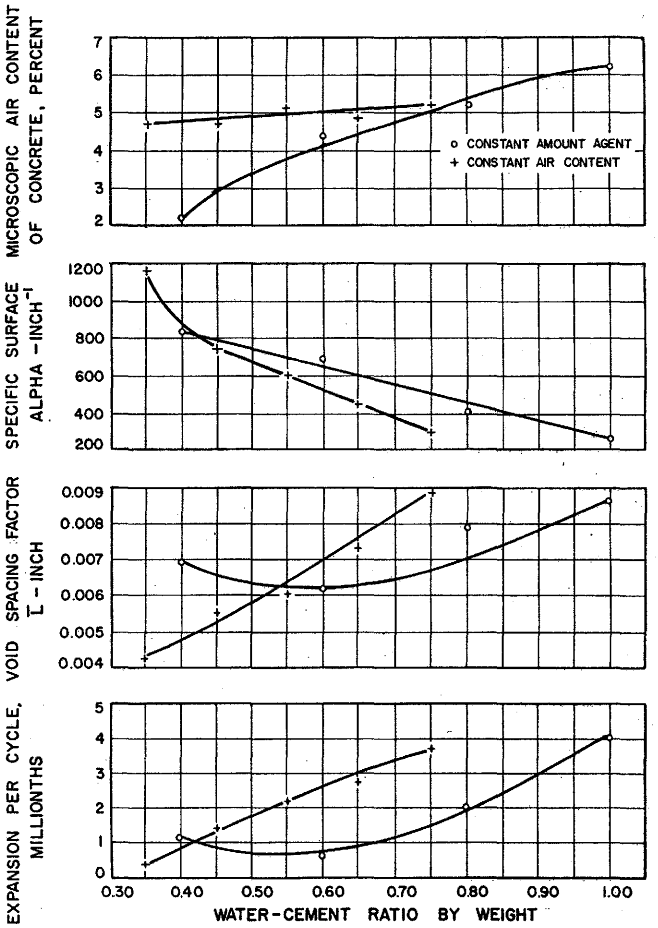

Figure 5. Effects of water-cement ratio on parameters of air void systems and freezing and thawing resistance of concrete containing either a constant amount of air-entraining agent or a constant amount of air (figure taken from Reference 19).

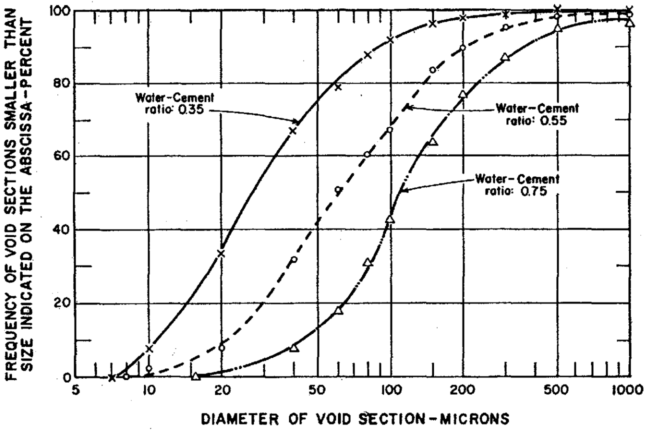

Figure 6. Change of distribution of void section size with change of water-cement ratio at similar air content (figure taken from Reference 19).

From Figure 6 it is seen that approximately 75 percent of the void sections are 50 microns or less in diameter for the concrete of low water cement ratio (.35), whereas only about 12 percent of the voids are in this size range in the concrete of high water-cement ratio (.75).

The change in void distribution is quantitatively illustrated in Table II.

With an increase in water-cement ratio from .35 to .55, the number of voids per cubic inch of concrete decreases from about 7,150,000 to about 2,470,000. At a water-cement ratio of .75 the concrete contains only about 700,000 voids per cubic inch. Also, voids less than 20 microns in diameter constitute 58 percent of the total number of voids at a water-cement ratio of .35 and only nine percent of the voids at a water-cement ratio of .75. With water-cement ratios of .35 and .55 most of the voids are less than 20 microns in diameter, whereas at a water-cement ratio of .75 most of the voids are between 20 and 40 microns.

From the above considerations, the following conclusions may be made concerning the effect of the water-cement ratio on the air void system of air-entrained concrete:

1. Increasing the water-cement ratio results in a reduction of the specific surface area of the air void system.

2. An increase of the water-cement ratio increases the air content of the cement paste.

3. Increasing water-cement ratio increases the percentage of large voids and decreases the total number of voids.

Properties of the Solids in the Concrete Mixture

Scripture, Hornibrook, and Bryant (17) reported that in mixes employing sand alone, the amount of air entrained is markedly affected by the gradation of the sand. They found that the amount of air entrained rises with decreasing size of the sand to a maximum for the size 28-48 mesh, thereafter decreasing rapidly. In mortar, they reported that the same trend was observed, but to a lesser degree and that the sand gradation at which maximum air-entrainment was obtained moved toward the coarser sizes. They also concluded that in concrete mixtures the effect of the sand is further suppressed. According to Powers (16), aggregate gradation and air entrainment are related inasmuch as void size and void content of the aggregate are functions of gradation. Powers states that,

> ". . . the aggregate provides a screen that holds bubbles when the cement is absent, or that holds bubbles in plastic concrete when no air-entraining agent is used; and its voids, slightly dilated, provide the space for paste and bubbles. Therefore, the relationship between air content of a given mixture and aggregate characteristics is determined by whether or not emulsification is the major entraining process, as well as by aggregate void content in the dilated state, and sometimes by void size. The latter two factors are functions of size range and grading; for a given size range, aggregate characteristics vary with grading. If grading of aggregates for a given mix is changed by increasing the proportion of a given size group a change in air content of the mixture may be obtained, and thus the change in the air content seems to be the effect of the particular size group that was increased. But, the effect actually is due to change in void content of the aggregate, and possibly to change in void size."

Powers has shown that as the size ratio (ratio of the mean size of the fine aggregate to the mean size of the coarse) of aggregate mixtures increases, the voids are enlarged and there is an increase in total aggregate void content.

Singh (18) has published work on the relation of aggregate gradation to air entrainment, some of which is shown in Table III. The gradings are shown along with the air contents of two different concrete mixtures with and without an air-entraining agent. The last four columns of Table III show that with or without the air-entraining agent the amount of air retained by a given mixture was greater the greater the size ratio of fine to coarse aggregate. Bubble sizes were not reported, but according to Powers (16),

> ". . . it is safe to say that the maximum size of bubble increased as the screen size increased. It should be noted also that the increase of air content due to the agent was about three percent in most cases, regardless of the total air content."

Mielenz et al. (19) have reported that in mortar batches made with sands of fineness moduli from 2.00 to 3.26, no appreciable variation in the air void system was observed.

Mielenz also reports that,

> ". . . it appears that the influence of the sand grading on the air void system, although generally apparent, may be appreciable only in very lean mixes and, from a practical point of view, may be ignored in the richer mixes since a relatively large amount of cement fines, with adequate air, seems to insure a good void system."

Mielenz has further reported that surface roughness of sand particles has some influence on the size of the air voids. In mixes containing sand of a rough surface texture the average specific surface area of voids was found to be 1037 in.$^{-1}$, while for the smoother sands, an average specific surface area of 742 in.$^{-1}$ was observed.

Investigations by Scripture, Benedict, and Litwinowicz (20) have shown that as specific surface area of cement increases, the amount of air entrained by an air-entraining agent is reduced. Little effect on air-entrainment was observed in mixes containing no agent.

Data presented by Bruere (21) substantiate the fact that air contents of pastes vary widely with the type of cement, and further that the specific surface area of bubbles varies only slightly with the type of cement used.

The effect of calcium chloride on the air void system is relatively unexplored. Mielenz (19) reported that addition of one percent calcium chloride by weight of cement resulted in a void system with larger bubbles (smaller specific surface area of bubbles) while Bruere (21) reported that additions of two percent by weight of cement resulted in little change in the air void system.

The following conclusions may be made concerning the effect of the solid materials on the air void system.

1. If size ratio is defined as the ratio of the mean size of the fine aggregate to that of the coarse, then with or without an air-entraining agent, the amount of air retained by a given mixture increases with increasing size ratio.

2. Wide differences in air content result from the use of different cements, but there appears to be little effect on the specific surface area of the bubbles.

Manipulation and Consolidation of Concrete

The duration and speed of the stirring or kneading procedure affect the air void system in such a way as to cause an increase in the air content and specific surface area of the voids as mixing time and speed increase. This is illustrated by data presented in Table IV and Table V. Using a given dose of air-entraining agent, Bruere (22) found that during prolonged mixing at constant speed, air content increased rapidly at first and then slowly approached an upper limit, as shown in Figure 7, diagram A. He also found that more air is accumulated the faster the mixture is stirred. This is illustrated in Figure 7, diagram B.

Powers (23) points out that,

> ". . . the kind of stirring device as well as its mode of operation have a significant effect on the amount of air entrained in cement paste; and, with any given device and mode of operation, rate of air accumulation is smaller the larger the batch since only a fraction of the batch is being subjected to effective stirring or kneading at a given time, and this fraction is usually smaller the larger the batch."

The handling and manipulation of air-entrained concrete acts to diminish the air content while the specific surface area of the bubbles increases. This is illustrated in data obtained by Mielenz et al. (19) and shown in Table VI.

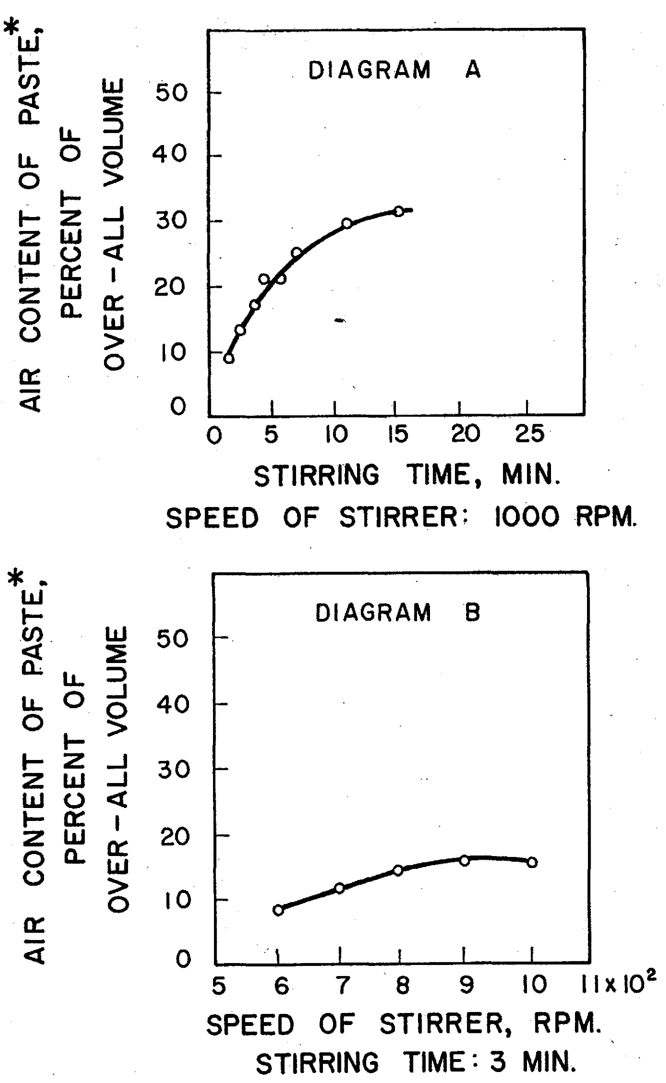

Figure 7. Effects of stirring time and speed of stirrer on air content of neat paste (figure taken from Reference 22).

Higginson (24) found that regardless of the amount of air originally entrained in laboratory specimens, all but about one percent could be removed from the specimens through vibration. He reports that with an initial air content of nine percent, one-half of the air could be removed from a .5 cubic ft. sample in a standard unit weight measure with 50 seconds of vibration, whereas removal of half of the air in a .2 cubic ft. sample required about 12 seconds vibration time. In tests made during construction of concrete dams, where the concrete was handled in large batches and placed in massive sections by vibration, Higginson found practically no loss of air during transport and final vibration. This observation seems in agreement with laboratory findings just mentioned; since the dam construction concrete was handled in large quantities, it is not surprising to find the loss of air reduced to a negligible level. Powers (23) points out that smaller quantities of concrete such as used for pavement slabs, may exhibit losses of air that

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**Air-entraining agent: sodium dodecyl sulfate; dose: 0.0125 percent by weight of cement.*

are not negligible, although it is doubtful that losses as high as those observed in laboratory concrete would result. Higginson concluded that the large rates of loss under laboratory conditions were due to intensification of vibration from the walls of the container.

Vibration influences concrete in such a way as to fluidize the paste. Therefore, for the small quantities of concrete confined in laboratory molds, conditions are enhanced for escape of bubbles, preferentially the larger, more buoyant ones. At the same time however, new air may be emulsified or air already present may be further divided into smaller bubbles. The final results would therefore be a leveling off of air content at some lower value and eventual loss of all but the smaller bubbles, hence increasing the specific surface area of the remaining bubble system.

The preferential loss of larger bubbles is illustrated in Table VII. The total number of voids per cubic centimeter of concrete is indicated to decrease from about 303,000 to about 120,000, and the number of voids smaller than 40 microns decreased only from 83 to 82 percent of the total number of voids in the concrete in each condition. The number of voids greater than 60 microns is greatly reduced in frequency by additional vibration.

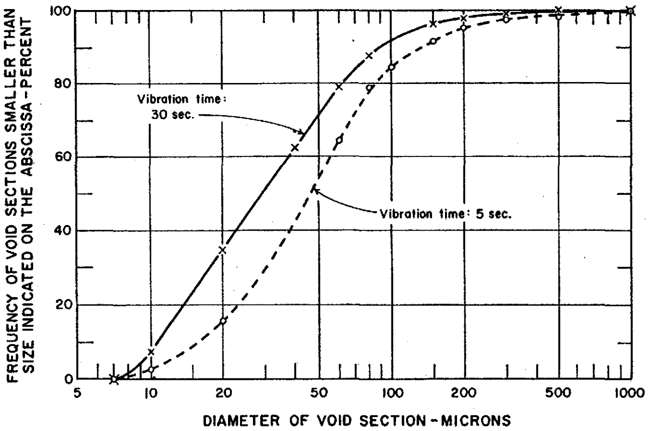

Figure 8. Change of distribution of void section size with change of duration of vibration (figure taken from Reference 19).

The increase in specific surface area of the voids with increased vibration is demonstrated in Figure 8 by additional vibration of 25 seconds, void sections larger than 90 microns are reduced from 19.5 to 11.0 percent of the total number of voids, and void sections smaller than 50 microns are increased from 55.0 to 72.0 percent of the total number.

Indications are that losses of air from air-entrained concrete during handling have desirable consequences provided a sufficient amount of air was initially present to insure protection from freeze-thaw damage. Mielenz et al. (19) give the following example: When the air content of a certain concrete mixture was reduced from 6.7 to 1.2 percent by vibration, the number of bubbles was reduced from 905,000 to 434,000. However, the remaining number apparently was adequate since the results of freezing and thawing tests were such as to indicate a high degree of protection with either number. At the same time, the 28-day compressive strength of the concrete containing the lesser number of bubbles showed an increase of 1000 psi over that of the concrete with the larger number of bubbles.

The following observations concerning the influence of manipulation and compaction of air-entrained concrete may be made:

1. With increasing mixing time and speed, higher air contents and specific surface areas of the resulting void systems are obtained.

2. The size of the sample being subjected to vibration plays a significant part in the effect vibration has on the resulting air system. Large quantities of air may be removed from small laboratory specimens by relatively minor vibration, whereas vibration affects the air system of massive concrete pours very little.

3. When air is lost from air-entrained concrete through handling and manipulation, the resulting concrete contains fewer bubbles. Those remaining are predominantly small and appear to be adequate in protecting the concrete from damage by freeze-thaw.

6. New Technology Needed to Promote the Achievement of Desirable Entrained Air Systems

The foregoing review of present knowledge of entrained air systems in concrete has illustrated the desirability for research in several areas which are outlined below:

1. A study of the effectiveness of present field practices in achieving a desirable air void system.

2. The development of a field test to determine the quality of an entrained air system (to supplement existing tests which measure only the quantity).

3. The effects of various combinations of air-entraining agents, retarders and mixing methods on the air void system.

4. A study of practical batching, placing and finishing methods with regard to their effect on the air void system.

Work is being conducted at the present time by the Structural Research Department of the Texas Transportation Institute in all of the areas listed and reports will be forthcoming.

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Appendix Tables

TABLE I. EFFECT OF AIR-ENTRAINING ADMIXTURES ON THE VOID SYSTEM IN CONCRETE*

Air-entraining admixture	Quantity of air-entraining admixture per cu yd of concrete	Water-cement ratio by weight	Air content, percent, by pressure method	Void parameters determined microscopically					Freeze-thaw expansion per cycle, millionths
				Air content, percent	Chord intercept, in.	Specific surface, in.$^{-1}$	Voids intercepted per in.	Spacing factor, $\bar{L}$, in.	
A	110 ml	0.45	5.6	5.9	0.0042	952	14.22	0.0046	0.0
B (solution)	1032 ml	0.45	4.9	3.5	0.0048	833	7.40	0.0066	0.0
B (powder)	111 g	0.45	4.8	4.8	0.0059	678	8.05	0.0071	0.0
C	147 ml	0.45	5.1	4.6	0.0045	889	10.14	0.0058	0.4
D	109 ml	0.45	5.4	5.1	0.0035	1143	14.57	0.0040	0.0
E	1176 ml	0.45	4.9	5.0	0.0061	656	8.19	0.0073	0.0
F	1838 g	0.45	4.6	5.2	0.0061	656	8.48	0.0071	0.1
G	738 g	0.45	5.1	4.1	0.0065	615	6.28	0.0082	0.0
H	3665 ml	0.45	4.7	3.4	0.0050	800	6.87	0.0071	0.2
I	9398 ml	0.45	2.7	2.8	0.0089	449	3.08	0.0139	
J	770 ml	0.45	5.1	4.0	0.0038	1050	10.43	0.0051	0.0
K	2192 ml	0.45	5.0	5.8	0.0058	690	9.85	0.0065	0.1
L	411 ml	0.45	4.8	2.3	0.0084	476	2.74	0.0140	6.0
B (solution)	52 ml	0.65	4.9	5.7	0.0063	635	9.05	0.0062	0.0
J	204 ml	0.65	4.7	5.2	0.0051	784	10.19	0.0055	0.0
L	300 ml	0.65	4.8	5.9	0.0112	357	5.26	0.0101	60.0

*Paste content 24.4 to 26.3 percent for W/C = 0.45 and 21.2 to 22.5 percent for W/C = 0.65. Table from Reference 8.

TABLE II. EFFECT OF WATER-CEMENT RATIO ON THE SIZE DISTRIBUTION OF VOIDS IN CONCRETE OF NEARLY CONSTANT AIR CONTENT

Diameter of voids, microns	Number of voids per cu cm of concrete*		
	W/C = 0.35	W/C = 0.55	W/C = 0.75
20	255,234	73,240	4,000
40	128,386	39,685	20,661
60	26,035	16,285	7,878
80	13,183	8,191	3,234
100	7,348	5,215	1,589
120	1,847	4,002	1,103
140	1,354	889	694
160	812	832	531
180	639	523	779
200	1,271	1,381	1,672
250	118	129	196
300	33.7	120	136
350	15.3	61.1	118
400	59.8	94.2	57.9
450	47.7	54.1	31.8
500	68.4	104.0	79.5
600	4.3	14.9	18.2
700	3.1	17.8	17.8
800	20.3	1.6	1.7
900		1.3	1.3
1000		9.7	8.7
2000		1.0	2.0
3000			
4000			
Total	436,479.6**	150,851.7**	42,810.9**

*Calculated in accordance with the method established by Lord and Willis.

**Corresponding numbers of voids per cu in. of concrete are 7,153,890; 2,472,447; and 701,655, respectively.

Table taken from Reference 19.

TABLE III. EXAMPLE OF EFFECT OF CHANGE OF AGGREGATE GRADING ON AIR CONTENT

Grading No.	Aggregate grading, percent in size-group indicated							Air content, percent			
	Fine aggregate (by sieve numbers)					Coarse		1:4.5 Mix, by wt, w/c = 0.45		1:6 Mix, by wt, w/c = 0.55	
	100-50	50-30	30-16	16-8	8-4	4-⅜"	⅜"-¾"	No Agent	With Agent	No Agent	With Agent
1	25.4						74.6	0.3	2.2	0.3	2.9
6	24.0					38.0	38.0	1.0	2.9	0.8	3.4
2	15.4	15.4				34.6	34.6	1.0	3.9	1.9	5.0
3	12.9	12.9	12.9			30.6	30.7	1.6	4.7	2.9	5.8
4	11.7	11.7	11.7	11.7		26.6	26.6	1.8	4.9	3.0	7.0
5	11.2	11.2	11.2	11.2	11.2	22.0	22.0	2.0	5.4	3.4	6.3

Table taken from Reference 18.

TABLE IV. EFFECT OF DURATION OF STIRRING ON AIR CONTENT AND SPECIFIC SURFACE AREA OF BUBBLES IN NEAT CEMENT PASTE

Stirring period, minutes	Air content, per cent	Specific surface area, α	
		in^2/in^3	cm^2/cc
1	13.6	1470	579
3	21.4	1760	693
4	21.4	1830	720
7	26.4	1940	764
15	26.7	2000	787

Notes:

w/c = 0.45.

Agent: Sodium dodecyl sulphate, 0.025 per cent of cement.

Table taken from Reference 21.

TABLE V. INFLUENCE OF SPEED OF STIRRER ON SPECIFIC SURFACE AREA OF BUBBLES PRODUCED IN NEAT CEMENT PASTE

Speed of stirrer, rpm	Air content, per cent	Specific surface area, α		Mean sp. surface diameter, microns
		$\frac{in^2}{in^3}$	$\frac{cm^2}{cc}$	
750	13.7	1230	484	124
1000	21.4	1760	693	87
1200	20.3	2150	846	71

Notes:

w/c = 0.45.

Agent: Sodium dodecyl sulfate, 0.025 per cent of cement. Mixing time 3 minutes, temperature 20-22°C.

Table taken from Reference 21.

TABLE VI. EFFECT OF HANDLING AND MOLDING ON THE VOID SYSTEM OF CONCRETE

Source of sample	Void parameters determined microscopically						
	Air content, percent	Chord intercept, in.	Specific surface, $in.^{-1}$	Voids intercepted per in.	Paste-air ratio	Paste content, percent*	Spacing factor, $\bar{L}$, in.
Natural gravel coarse aggregate, low air content							
Mixer	7.8	0.0135	296	5.775	3.04	23.74	0.0103
Unit weight can	3.4	0.0095	421	3.578	7.31	24.88	0.0130
Slump cone	2.9	0.0090	444	3.221	8.62	25.01	0.0135
Hand rodded bar	2.3	0.0071	563	3.238	10.94	25.16	0.0117
Vibrated cylinder	2.2	0.0065	615	3.384	11.45	25.19	0.0110
Natural gravel coarse aggregate, high air content							
Mixer	10.3	0.0065	656	16.884	2.23	22.92	0.0034
Unit weight can	7.8	0.0053	755	14.716	3.02	23.56	0.0040
Slump cone	7.1	0.0051	784	13.921	3.34	23.74	0.0043
Hand rodded bar	6.3	0.0046	870	13.694	3.80	23.94	0.0044
Vibrated cylinder	5.7	0.0039	1030	14.614	4.23	24.09	0.0041
Crushed limestone coarse aggregate, high air content							
Mixer	13.5	0.0057	702	23.658	1.70	22.94	0.0024
Unit weight can	8.5	0.0045	889	18.887	2.86	24.27	0.0032
Slump cone	8.4	0.0043	930	19.534	2.89	24.29	0.0031
Hand rodded bar	7.3	0.0040	1000	18.250	3.37	24.59	0.0034
Vibrated cylinder	6.5	0.0032	1250	20.312	3.82	24.80	0.0031

*Corrected for air content of the concrete.

Table taken from Reference 19.

TABLE VII. EFFECT OF INTERNAL VIBRATION ON VOID SIZE DISTRIBUTION IN CONCRETE

Diameter of voids, microns	Number of voids per cu cm of concrete*	
	2 sec vibration	50 sec vibration
20	155,839	68,869
40	96,180	29,887
60	19,830	15,641
80	14,666	2,981
100	6,014	1,836
120	5,847	838
140	1,855	491
160	884	306
180	772	265
200	418	180
250	525	70.1
300	139	19.1
350	65.6	2.0
400	45.0	20.4
450	23.9	23.0
500	18.2	5.7
600	4.1	0.6
700	12.7	3.6
800	7.4	
900	1.8	
1000	13.9	
2000	0.6	
3000	0.7	
4000	0.2	
Total	303,163**	121,438**

*Calculated in accordance with the method established by Lord and Willis.

**Corresponding numbers of voids per cu in. of concrete are 4,968,841 and 1,990,368, respectively.

Table taken from Reference 19.