Air Void Systems Affected By Chemical Admixtures and Mixing Methods

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Variations in the entrained-air system in hydraulic cement mortars due to different chemical types of air-entraining agents and retarders and different mixing methods were investigated. Twenty-seven mortar batches were prepared at a fundamentally constant air content using different combinations of 3 mixing sequences, 3 air-entraining agents, and 3 retarders.

The Powers and Philleo spacing factors were determined on specimens from each batch, and were used as the criteria for comparison of the air void systems. Observed differences in the Powers spacing factor were found to be statistically significant for different mixing methods and different air-entraining agents. Comparatively large values of the Powers spacing factor were observed when the air-entraining agent and retarder were combined in the same water phase before being combined with the cement and sand. Relatively low values of Powers spacing factor were observed when the organic acid retarder was used, regardless of the air-entraining agent used.

•THE practice of intentionally entraining air bubbles in concrete was introduced in the 1930's and has since become one of the most important developments in concrete technology.

The primary purpose of air entrainment in concrete is to protect the paste from the potentially destructive hydraulic pressures developed during the freezing of moisture contained within the concrete matrix. Work done by T. C. Powers (1) in 1954 predicted the order of magnitude of this pressure and showed that not only was the total volume of air contained in the concrete of importance, but more importantly the size distribution and frequency of air bubble voids must be such as to provide protection to the paste. Powers states that ". . . a body of nearly saturated paste more than a few hundredths of an inch thick cannot possibly be frozen rapidly without incurring damage."

To indicate the thickness of the paste, Powers introduced a factor defined as the maximum average distance from a point in the paste to the nearest air void (Powers spacing factor, $\overline{L}$). This factor is indicative of the distance water would have to travel during the freezing process in order to reach an air bubble void. According to Powers, if these voids are spaced sufficiently close, the internal hydraulic pressure created as a result of the movement of moisture would be sufficiently low and rupture of the paste in tension would not occur.

More recent laboratory observations have supported Powers' findings that for a particular air-entrained concrete, the magnitude of the spacing factor serves as an indication of that concrete's ability to withstand freezing and thawing. That is, as the magnitude of $\overline{L}$ for a given concrete decreases, the durability of the concrete subjected to freezing and thawing increases.

The magnitude of $\overline{L}$ is dependent on the frequency distribution of the void sizes in a given concrete mixture. Therefore, either the spacing factor or the frequency

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distribution of void sizes can be used as an indication of a concrete's durability when subjected to freezing and thawing.

The spacing factor proposed by Powers is not the only indication of a concrete's ability to withstand freezing and thawing. In 1955, R. E. Philleo (2) suggested a factor based on what he termed the protected paste volume concept. Larson et al (3) reported evidence sufficient to justify further studies of this factor as an indicator of the frost resistance of concrete. To determine the Philleo factor, it is necessary to obtain a bubble size distribution from which the total number of bubbles per unit volume of paste may be calculated. As stated (3): "This number is used to calculate a factor indicating the protected paste volume, termed the Philleo spacing factor. This 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 paste."

As with Powers spacing factor, the magnitude of the Philleo factor is dependent on the frequency distribution of void sizes.

Because of the preceding considerations, it is believed that, regardless of the factor or factors chosen to indicate a particular concrete's ability to withstand freezing and thawing, the frequency distribution of the void sizes is of primary importance in frost resistance. Previous investigations (4, 5) have shown that numerous factors influence the frequency and void distribution of the entrained-air system in both concrete and mortar. The work reported in this paper was undertaken to study the effects of the following factors on the entrained-air system of mortars:

1. Effects of different mixing sequences;
2. Effects of different air-entraining agents;
3. Effects of different retarders; and
4. Interaction effects of mixing sequences, air-entraining agents, and retarders.

It was not expected that the numerical differences could be extrapolated directly to concrete. However, the significant differences in the air void system of mortars would seem to indicate that some differences would be encountered due to the variation of the corresponding factors in concrete.

The criteria used to compare the differences in the air void systems were the magnitudes of the Powers and Philleo spacing factors. The spacing factors were not themselves under a comparative investigation.

TABLE 1

WATER-CEMENT RATIOS

Batch Designation	Water-Cement (wt water/wt cement)
AV-M2	0.550
AD-M2	0.550
AH-M2	0.564
(a) Mixing Sequence M1	
AV-RO	0.536
AD-RO	0.543
AH-RO	0.543
AV-RL	0.550
AD-RL	0.550
AH-RL	0.550
AV-RP	0.543
AD-RP	0.550
AH-RP	0.557
(b) Mixing Sequence M2	
AV-RO	0.509
AD-RO	0.509
AH-RO	0.509
(b) Mixing Sequence M2 (cont'd)	
AV-RL	0.543
AD-RL	0.550
AH-RL	0.550
AV-RP	0.522
AD-RP	0.522
AH-RP	0.543
(c) Mixing Sequence M3	
AV-RO	0.536
AD-RO	0.530
AH-RO	0.530
AV-RL	0.522
AD-RL	0.543
AH-RL	0.550
AV-RP	0.536
AD-RP	0.536
AH-RP	0.550

Figure 1. Determining flow of the hydraulic cement mortar.

Figure 2. Determining air content of the hydraulic cement mortar.

TESTING PROGRAM

The mortars used in these tests were composed of Atlas Type I cement, Ottawa standard graded silica sand (as defined in ASTM C 185-59) and water. The cement/sand ratio of all mortars was 0.366 and sufficient water and air-entraining agent was used to produce a flow of 75 percent and air content of 11 ±1 percent. Tests were conducted in accordance with ASTM C 185-59 except that the dimensions of the cylindrical container were $2\frac{7}{16}$ in. in diameter by $3\frac{21}{32}$ in. in depth. Eleven percent air in mortar corresponds to 6 percent in a concrete with 57 percent mortar by volume.

Water/cement ratios for the mortars are given in Table 1. The procedure to determine the flow and air content of the hydraulic mortar is shown in Figures 1 and 2.

Three air-entraining agents (AV, AD, AH) and three retarders (RO, RL, RP) were used in this testing program. In the designation used, A indicates an air-entraining agent and R, a retarder: the letter following A indicates the type of air-entraining agent (V—vinsol resin, D—synthetic detergent, H—organic salt of sulfonated hydrocarbon);

TABLE 2

MIXING PROCEDURES

Designation	Description
M1	Sand and cement were placed in the mixer and allowed to dry mix 1 min at 150 rpm. Air-entraining agent and retarder were combined in the mixing water and introduced into the mixer over a 1-min time period. Mortar was then mixed an additional 2 min at 340 rpm.
M2	Sand and cement were placed in the mixer and allowed to dry mix 1 min at 150 rpm. Air-entraining agent was combined with one-half the mixing water and added over a 30-sec period. Retarder was combined with the remainder of the water and added over a 30-sec period. Mortar was then mixed an additional 2 min at 340 rpm.
M3	Sand was placed in the mixer and one-half the mixing water containing the air-entraining agent was added over a 30-sec time period at a mixing speed of 150 rpm. Cement was then added over a 1-min period at a mixing speed of 150 rpm. Remainder of the mixing water containing the retarder was added over a 30-sec period. Mortar was then allowed to mix for 2 min at 340 rpm.

Figure 3. Technicians operating linear traverse device.

Figure 4. Sawing mortar specimen to expose surface for microscopic examination.

that following R indicates the type of retarder (O—organic acid, L—lignosulfonate, P—hydroxylated polymer).

Each air-entraining agent was used in combination with each retarder and three mixing sequences (M1, M2, M3—Table 2) were employed to yield 27 batches of mortar. With the exception of retarder RL, the manufacturer's recommended quantity was used. Because of the air-entraining characteristic of retarder RL, it was necessary to reduce the quantity to maintain the proper air content while using a significant amount of air-entraining agent.

The method used to determine the parameters of the air void system was essentially in accordance with ASTM C 457-66T, except that the Rosiwal linear traverse technique was modified in order to record each individual chord length. The apparatus used for measurement of the parameters is shown in Figure 3.

Information necessary to determine the Philleo spacing factor was obtained using the mathematical methods outlined by Larson et al (3). To facilitate the tedious numerical analysis necessary to carry out this investigation, the data reduction was programmed for the IBM 7094 and IBM 1401.

From each mortar batch, a prismatic specimen was cast and allowed to moist cure for 14 days before being prepared for microscopic examination. Figure 4 shows the specimen being sawed to expose a surface approximately at right angles to the finished surface of the mortar. The exposed surface is then ground with silicon carbide abrasive (Fig. 5) until it is suitable for microscopic observation.

Figure 5. Grinding exposed surface with silicon carbide abrasive.

The air-void parameters of air content, specific surface area, and Powers spacing factor were determined in accordance with ASTM C 457-66T. Traverse lengths ranged from 50 to 60 in. on a surface of 9 sq in.

TEST RESULTS AND DISCUSSION

Using the method described by Lord and Willis (6), the number of voids per cubic centimeter in the 0 to 508 -μ range was determined as well as the total number in the 0 to 2,540 -μ range. The number of voids per cubic centimeter in the 0 to 508 -μ range was then determined using the mathematical approach described by Larson et al (3), thus enabling determination of the Philleo spacing factor. Table 3 summarizes the information of primary interest.

Effect of Mixing Sequences

The statistical technique used to determine the significance of the observed differences in the Powers and Philleo spacing factors was a three factor interaction analysis of variance. However, because there was no repetition of the batches, there is no guarantee that the estimate used for testing variation is not lower than the true variation.

The significance of the differences in the mean values was determined using Tukey's (7) h. s. d. procedure. The magnitudes of the Powers spacing factors are shown in Figure 6 for each mortar batch. Using a three factor interaction analysis of variance and the Powers factor as a criterion, a difference in mixing sequences significant at the 99 percent level was found to exist. The dashed lines shown represent the mean value of the spacing factors associated with each mixing sequence. It was found that between mixing sequences M3 and M1 and M2 and M1, the mean differences were significant at the 99 percent level with M1 giving larger values of Powers spacing factor. No significant difference was observed between M2 and M3. Therefore, a less desirable air-void system was evident in the mixing procedure where the admixtures were combined prior to their addition.

The same procedure was followed using the Philleo factor as a criterion for observing the effect of the mixing sequence. Although the magnitudes of this factor are not shown in graphical form, they are given in Table 3. Table 4 summarizes the mean

TABLE 3

PARAMETERS OF THE AIR VOID SYSTEM

Batch Designation	Microscopic Air Content (%)	Powers Spacing Factor (in.)	Philleo Spacing Factor (in.)	Specific Surface Area (in.$^{-1}$)	No. Bubbles/CC Mortar, 0-508-μ Range (3)	No. Bubbles/CC Mortar, 0-508-μ Range (6)
AV-M2	13.56	0.00565	0.00359	520	137,251	93,319
AD-M2	14.15	0.00771	0.00615	358	27,454	17,669
AH-M2	11.47	0.00611	0.00362	581	131,188	74,964
AV-RO-M1	15.75	0.00574	0.00567	420	31,355	45,629
AD-RO-M1	10.55	0.00815	0.00418	471	74,406	30,092
AH-RO-M1	8.67	0.00806	0.00356	557	94,044	41,772
AV-RL-M1	11.52	0.00888	0.00503	394	53,667	25,504
AD-RL-M1	11.84	0.01173	0.00514	289	47,407	8,618
AH-RL-M1	8.16	0.00954	0.00399	486	111,321	27,502
AV-RP-M1	13.63	0.00786	0.00519	365	52,431	39,697
AD-RP-M1	15.12	0.00837	0.00736	306	16,379	13,254
AH-RP-M1	8.80	0.01032	0.00579	434	42,357	41,420
AV-RO-M2	13.48	0.00645	0.00330	442	181,449	46,062
AD-RO-M2	13.50	0.00805	0.00550	353	40,560	25,124
AH-RO-M2	10.92	0.00600	0.00220	603	384,774	97,720
AV-RL-M2	12.52	0.00830	0.00521	382	39,278	24,674
AD-RL-M2	12.30	0.00931	0.00422	349	75,793	16,891
AH-RL-M2	10.21	0.00646	0.00344	620	154,309	78,478
AV-RP-M2	11.67	0.00688	0.00349	493	172,164	98,625
AD-RP-M2	11.16	0.00890	0.00505	400	57,123	38,025
AH-RP-M2	10.69	0.00755	0.00420	502	99,701	77,662
AV-RO-M3	11.16	0.00794	0.00481	452	64,799	49,605
AD-RO-M3	16.35	0.00708	0.00497	325	45,665	19,703
AH-RO-M3	11.00	0.00729	0.00347	498	145,312	51,414
AV-RL-M3	13.74	0.00721	0.00617	390	24,574	22,340
AD-RL-M3	12.51	0.00833	0.00547	381	40,414	21,061
AH-RL-M3	10.51	0.00569	0.00190	667	597,374	107,200
AV-RP-M3	11.38	0.00725	0.00344	484	154,537	38,667
AD-RP-M3	11.38	0.00779	0.00425	452	82,886	41,491
AH-RP-M3	10.57	0.00802	0.00444	480	87,397	63,365

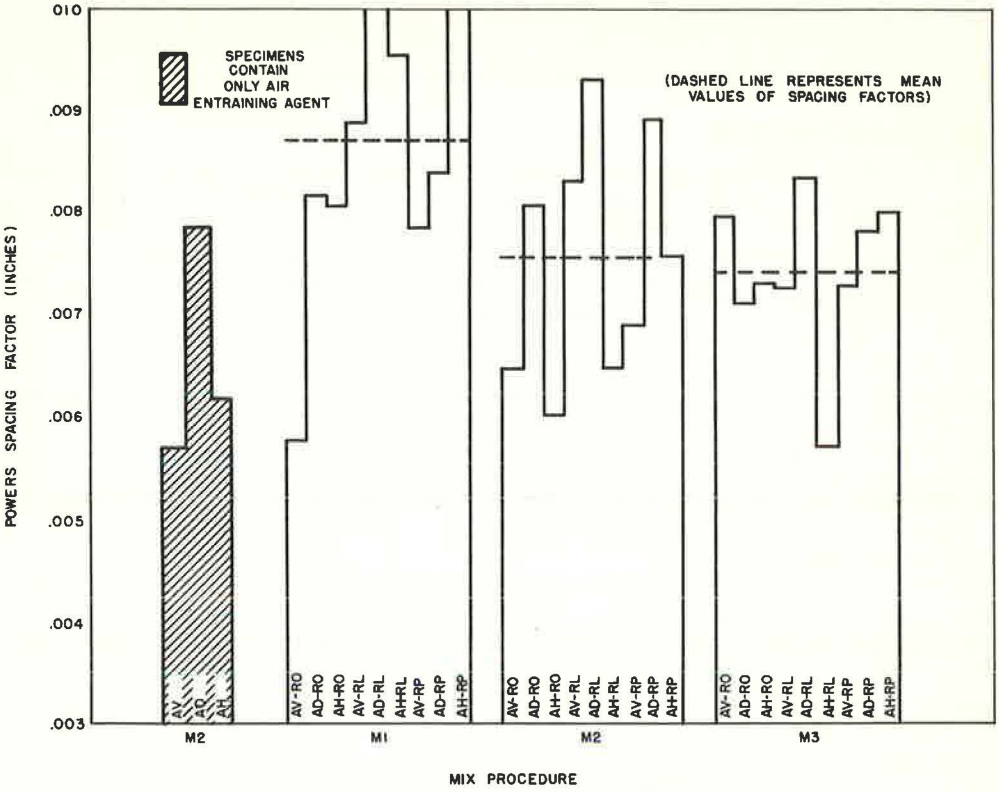

Figure 6. Comparison of Powers spacing factor between mixing procedures.

values. Using the Philleo factor as the criterion, no significant difference was indicated between mixing sequences.

Effect of Air-Entraining Agents

The effectiveness of the air-entraining agents was investigated using the same tests for significance. It was found that significant differences existed between the air-entraining agents. Air-entraining agent AD produced an air void system which yielded higher values of both the Philleo and Powers spacing factor. No significant difference was observed between agents AV and AH, whereas the differences in the average Powers spacing factors of AV and AD, and AH and AD were significant at the 99 percent and 95 percent levels, respectively. Mean values of Powers factor are shown in Figure 7.

Using the Philleo factor, a significant difference in the means of AD and AH was indicated at the 95 percent level.

TABLE 4

SUMMARY OF MEAN VALUES OF POWERS AND PHILLEO SPACING FACTORS

Mean Spacing Factor	Powers Spacing Factor (in.)			Philleo Spacing Factor (in.)		
Mixing procedure	M1	M2	M3	M1	M2	M3
	0.00874	0.00754	0.00740	0.00510	0.00407	0.00432
Air-entraining agent	AV	AD	AH	AV	AD	AH
	0.00739	0.00863	0.00766	0.00470	0.00513	0.00367
Retarder	RO	RL	RP	RO	RL	RP
	0.00720	0.00838	0.00810	0.00418	0.00451	0.00480

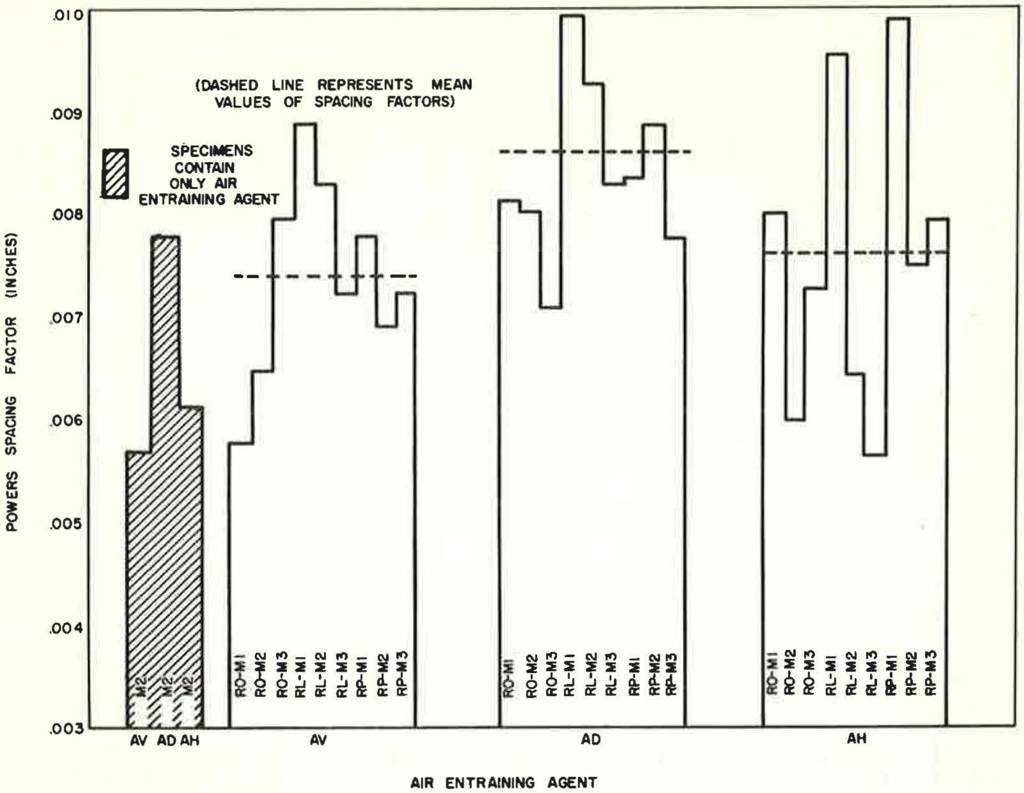

Figure 7. Comparison of Powers spacing factor between air-entraining agents.

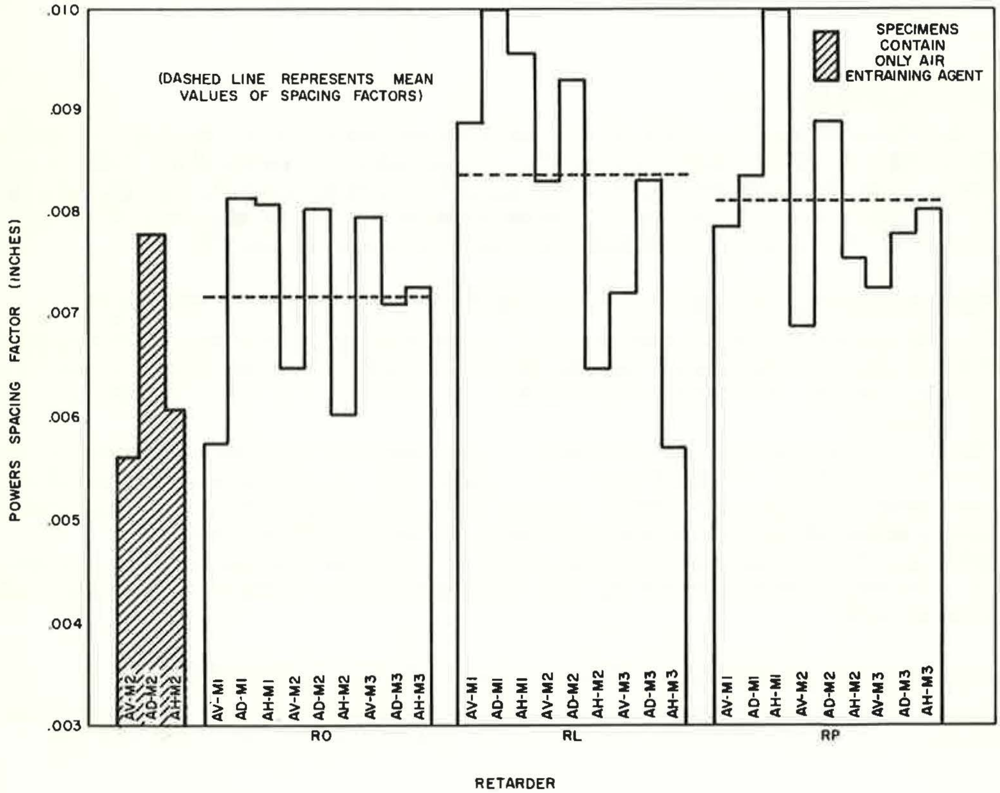

Figure 8. Comparison of Powers spacing factor between retarders.

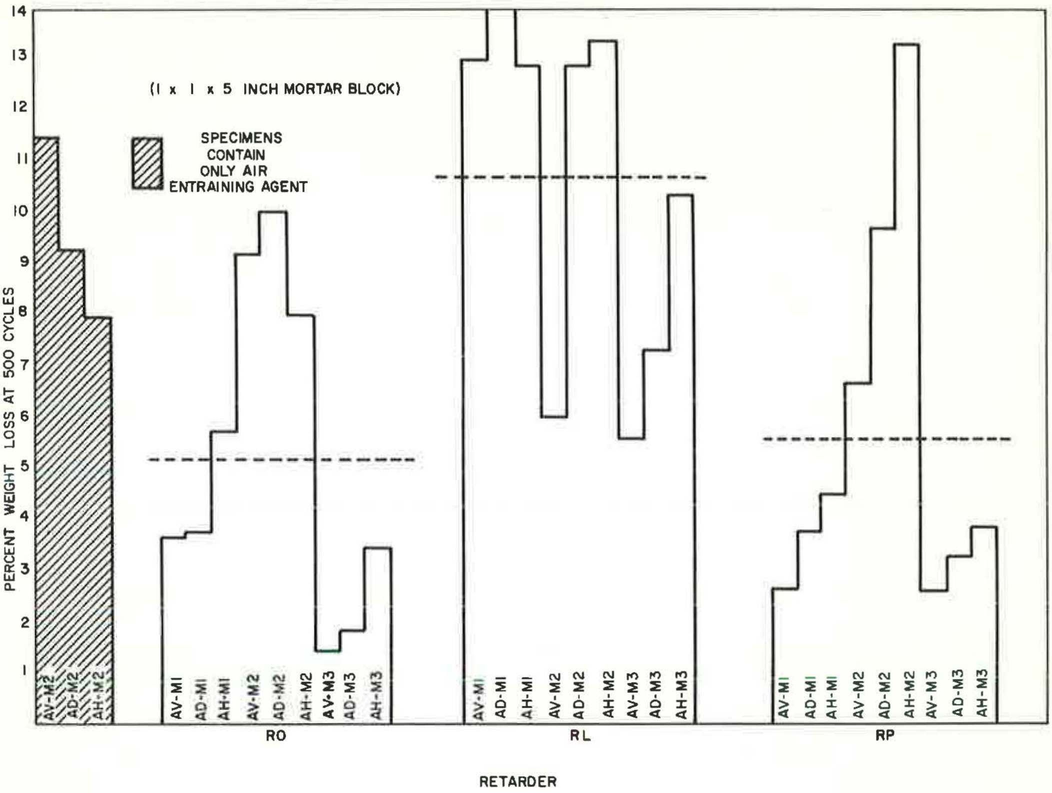

Figure 9. Comparison of freeze-thaw weight loss between admixtures.

Effect of Retarders

A significant difference at the 99 percent level existed between different combinations of retarders and air-entraining agents when compared on the basis of the Powers spacing factor (Fig. 8). The difference in the mean values of RO and RL was significant at the 99 percent level, whereas the difference between RO and RP showed a 95 percent significance. No significant difference was noted between RP and RL.

Interaction Effects of Mixing Sequences, Air-Entraining Agents and Retarders

The interaction of mixing sequences, air-entraining agents and retarders was found to produce values of the Powers spacing factor with differences significant at the 95 percent level; however, no significance was found to exist between different values of the Philleo factor.

When both retarders and air-entraining agents were used, introduction into the batch in accordance with the method described in mixing sequence M1 was least desirable.

With the three mixing procedures and the three retarders used, it was found that air-entraining agent AD performed less satisfactorily than did AV and AH.

Under the three conditions of mixing and in combination with the three air-entraining agents, retarder RO was found to be less detrimental to the development of a desirable air-void system.

Resistance of Mortar to Deterioration as a Result of Freezing and Thawing

Two 1 by 1 by 5-in. mortar specimens were cast from each mortar batch. These specimens were moist cured for 14 days in 100 percent relative humidity and then

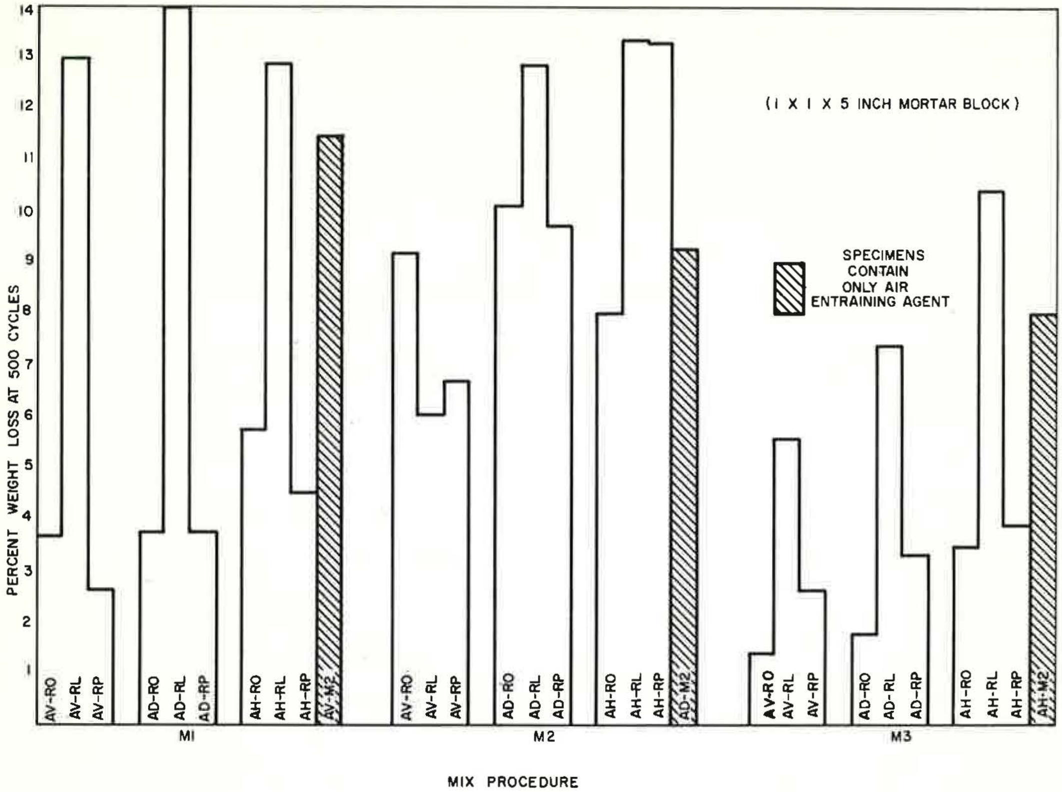

Figure 10. Comparison of freeze-thaw weight loss between air-entraining agents and mixing methods.

subjected to rapid freezing and thawing in water in accordance with ASTM C 290-63T. Weight loss of the specimens was progressively recorded until termination at 500 cycles.

It has not been shown that weight loss in mortar is a good criterion for predicting concrete freeze-thaw durability. However, significant discernible trends do seem apparent between the air-entraining agents and retarders (Fig. 9) and mixing procedures. One indication of correlation between this test and concrete freeze-thaw durability, as indicated by loss in resonant frequency, is shown by observing the similarity of these differences between retarders and the differences shown in Research Report 70-3 (8).

Data in Figure 10 indicate lower weight losses occur in those specimens mixed in accordance with procedure M3.

CONCLUSIONS

1. Of the three mixing procedures, significantly larger values of the spacing factor were found in mortars where the air-entraining agent and retarder were mixed in the same water phase and introduced into the sand and cement (M1, Table 2).

2. The air-entraining agents investigated differed in their abilities to produce a system of closely spaced air voids. The vinsol resin (AV) and the organic salt of sulfonated hydrocarbon (AH) produced an entrained-air system of closely spaced voids as indicated by the smaller values of the spacing factors.

3. The lignosulfonate (RL) and hydroxylated polymer (RP) retarders, used in combination with the three air-entraining agents, produced systems of voids with larger spacing factors than did the organic acid retarder (RO) when used with the same air-entraining agents.

4. Lower weight losses due to freezing and thawing were observed in mortar specimens which were mixed by first introducing the air-entraining agent and one-half the mixing water into the sand and blending before adding the other constituents (M3, Table 2).

5. Comparatively larger values of weight loss due to freeze-thaw were observed in mortar specimens containing the lignosulfonate retarder (RL).

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