INVESTIGATION OF CONCRETE MIXTURES INCORPORATING HOLLOW PLASTIC MICROSPHERES

by

H. Celik Ozyildirim
and
Michael M. Sprinkel
Research Scientists

(The opinions, findings, and conclusions expressed in this report are those of the authors and not necessarily those of the sponsoring agencies.)

Virginia Highway & Transportation Research Council
(A Cooperative Organization Sponsored Jointly by the Virginia Department of Highways & Transportation and the University of Virginia)

In Cooperation with the U. S. Department of Transportation
Federal Highway Administration

Charlottesville, Virginia

July 1981
VHTRC 82-R7

CONCRETE RESEARCH ADVISORY COMMITTEE

SUMMARY

This study investigated the potential of hollow plastic microspheres, HPM, for providing non-air-entrained portland cement concrete resistance to damage from cycles of freezing and thawing. In the study, a mixture with an air-entraining agent (vinsol resin) was used as the control for comparison with three experimental mixtures — one with HPM, one with super water reducers (SWR) and HPM, and one with fly ash and HPM.

HPM mixtures at dosages of 1.5% or more by weight of cement exhibited satisfactory resistance to damage from cycles of freezing and thawing. Mixtures with SWR and HPM exhibited low durability factors and failed the acceptance criterion requiring a durability factor of 60 or more. Concretes with fly ash and HPM displayed durability factors comparable to those of mixtures with the same dosages of HPM. However, the weight losses of fly ash mixtures were higher than those of comparable mixtures.

To determine the cause of low durability factors in mixtures with SWR and HPM, specimens were examined using an optical microscope and scanning electron microscope. It was found that the paste of the mixture without the SWR contained numerous well-distributed HPM voids. The paste of mixtures with the SWR and the same dosage of HPM contained few HPM voids distributed throughout, but did have concentrations of HPM at the undersurface of the aggregates.

TABLE OF CONTENTS

INVESTIGATION OF CONCRETE MIXTURES INCORPORATING HOLLOW PLASTIC MICROSPHERES

by

H. Celik Ozyildirim
and
Michael M. Sprinkel
Research Scientists

INTRODUCTION

Air entrainment is universally used to protect concrete from the adverse effects of freezing and thawing, but to be effective the air voids should be spaced closely and uniformly. A spacing factor of 0.008 in. (0.20 mm) or less is a well-established criterion for the protection of ordinary portland cement concretes. The air-entrained voids accommodate the movement of the water in saturated concrete undergoing freezing so that the pressure buildup caused by expanding water does not reach a level that will produce adverse effects.

The presence of certain chemicals in portland cement; the processes used in producing the concrete, particularly mixing; the mixing temperatures; the quantity of mixing water; and the composition and quantities of ingredients other than cement affect the performance of the air-entraining admixture and thus the generation of bubbles in concrete. For example, the use of super water reducers (SWR) in concrete alters the air void system by causing the bubbles to be larger than desirable. In concretes containing fly ash, difficulties are encountered in attaining the proper amount of air entrainment because of the chemical and physical characteristics of fly ash.[1]

Compared to past requirements, high (5% to 8%) air contents are currently considered desirable for the long-term durability of bridge decks, and consequently higher amounts of air-entraining admixtures are being used. As a result, the difficulties that may arise from the factors listed above are compounded. The concern about these problems is reflected in the recent programming of the National Cooperative Highway Research Program project titled "Control of Entrained Air in Concrete".[2] This project will seek practical means for controlling air entrainment in structural concrete at the 5% to 8% levels.

In addition to the difficulties cited above, the air voids resulting from high levels of air entrainment lower the strength of concrete. Thus any other means of relieving the hydraulic pressures caused by the expansion of water in concrete could be beneficial. Toward this end, the use of hollow plastic microspheres has been proposed as an alternative to air entrainment. According to a paper by Kaper, microspheres of approximately 30 μm diameter (marketed under the trade name "Kleenopor") relieve hydraulic pressure by accommodating the deformations caused by the expanding water as it freezes.(3)

OBJECTIVE AND SCOPE

The objective of this study was to determine whether Kleenopor hollow plastic microspheres (HPM) have a potential for improving the resistance of non-air-entrained portland cement concrete to damage from cycles of freezing and thawing.

Four types of mixtures were studied: a mixture with an air-entraining agent (vinsol resin) as a control; one with HPM; one with an SWR and HPM; and one with fly ash and HPM. For each type of mixture, batches were prepared with different dosages of HPM so as to gain an indication of the optimum dosage for a given type of mixture.

From 38 batches of concrete, 78 beams (typically 2 per batch) measuring 3 x 4 x 16 in. (75 x 100 x 400 mm) were prepared and subjected to rapid freezing and thawing tests, 76 (2 per batch) 6 x 12 in. (150 x 300 mm) cylinders were used to determine compressive strengths, and 27 slabs were cut from prisms and subjected to linear traverse analysis.

Rapid Freezing and Thawing Tests

ASTM Procedure C666 can be used to determine the resistance of concrete specimens to damage from cycles of freezing and thawing. The test specimens can be fabricated in the laboratory or cut from hardened concrete. Method C666 provides two procedures, A and B. Both procedures require a 14-day moist cure for the test specimens, and both require that they be subjected to rapid cycles of freezing and thawing. In procedure A, the cycles are run in water; in B, the freezing is done in air, the thawing in water. At certain intervals during the tests, weights and fundamental transverse frequencies are determined.

At the Research Council, a modified version of procedure A is followed in which the specimens are subjected to an additional 1-week air cure and the test water contains 2% NaCl. In addition to the weight and frequency measurements, the surface is rated in accordance with ASTM C672. The Council's acceptance criteria state that the average weight loss for three specimens should be 7% or less, the durability factor should by 60 or more, and the surface rating 3 or less.

Air Void Studies on Hardened Concrete

It is believed that in many cases it is also possible to predict the resistance of concrete specimens to damage from freezing and thawing by examining hardened concrete.

The three important parameters of the void system in hardened concrete are the total void content, the specific surface, α, and the spacing factor, $\bar{L}$. The specific surface is the surface area per unit volume of the bubble and indicates the average size of voids; the spacing factor indicates the average distance water must travel to reach a void.

ASTM C457 includes two methods for determining the above parameters: the linear traverse method and the modified point-count method. Both are based on microscopic examinations of lapped surfaces. The concrete is assumed to have satisfactory resistance to damage from cycles of freezing and thawing if α is larger than 600 $in.^{-1}$ (24 mm^{-1}) and $\bar{L}$ is smaller than 0.008 in. (0.20 mm).[4]

PLASTIC MICROSPHERES

HPM are offered for use in concrete subjected to cycles of freezing and thawing when saturated to eliminate the previously mentioned drawbacks of using an air-entraining admixture.

The HPM used in this study has an average diameter of 30 μm. Its specific gravity is 12.5 $lb./ft.^3$ (0.2 g/cm^3). The cost is expected to be $2 per lb. ($4 per kg) at this time, and a reduction in price is envisioned.

INITIAL TEST PROGRAM

The supplier had recommended the use of HPM at the dosage of 0.3% by weight of cement (HPM 0.3) and, consequently, an initial study of limited scope was conducted using this recommended dosage. Four types of mixtures were studied: a mixture with an air-entraining admixture (vinsol resin) as a control; one with HPM 0.3; one with SWR and HPM 0.3; and one with fly ash and HPM 0.3.

Sample Preparation and Testing

Utilizing the mixture proportions shown in Table 1, 1-ft.^{3} batches were prepared, and two 6 x 12 in. (150 x 300 mm) cylinders and three 3 x 4 x 16 in. (75 x 100 x 400 mm) prisms were fabricated from each batch.

For assurance, duplicate batches were prepared for each of the four mixtures with the exception of the super water reduced concrete, where a naphthalene sulfonate polymer admixture was used in the first batch and a melamine sulfonate polymer admixture in the second. The plastic properties of the fresh concrete are given in Table 2. The mixture data for two batches of non-air-entrained concrete, including one prepared with a naphthalene sulfonate polymer admixture, are also reported in Table 2 as mixtures 5 and 6. These batches were prepared at a different time using similar but different materials and were included in the study for comparative purposes. The non-air-entrained concrete had a cement content of 588 lb/yd.^{3} (349 kg/m^3) and a water/cement ratio (w/c) of 0.50. The non-air-entrained concrete prepared with the SWR admixture had a cement content of 658 lb/yd.^{3} (390 kg/m^3) and a w/c ratio of 0.39.

The cylinders were tested in compression after 28 days of moist curing. After a month of moist curing, one of the prisms from each batch was subjected to linear traverse analysis and the remaining ones were tested for resistance to cycles of freezing and thawing.

Table 1

Mixture Proportions Used by Weight Relative to Cement

Ingredient	Control with AEA	HPM 0.3	HPM 0.3 + SWR	HPM 0.3 + Fly Ash
Cement	1*	1*	1*	1**
Water	0.48	0.50	0.40	0.58
Coarse aggregate	3.31	3.31	3.31	3.96
Fine aggregate	1.85	2.06	2.32	2.19
Fly ash	0	0	0	0.20

*Cement content = 588 lb./yd.^{3} = 349 kg/m^3.

**Cement content = 506 lb./yd.^{3} = 300 kg/m^3.

Table 2

Plastic Properties of Concrete Mixtures Containing HPM
(Average of 2 Batches)

Mixture No.	Mix Variable	Slump, in.	Air Content, %[a]	Unit Weight,[b] lb./ft.^{3}
1	Control with AEA	4.0	6.3	140.0
2	HPM 0.3	2.6	1.6	146.4
3	HPM 0.3 + SWR	4.0	3.4	146.6
4	HPM 0.3 + Fly Ash	3.9	1.0	145.2
5	Non-AE[c]	1.7	2.6	147.0
6	Non-AE with SWR[c]	1.9	4.5	149.4

NOTE: 1 in. = 25 mm; 1 lb./ft.^{3} = 16 kg/m^3.

[a]Pressure method

[b]Determined using the pressure meter bucket (volume = 0.22 ft.^{3}) [6.2 dm^3]

[c]Only one batch

Results

The results of rapid freezing and thawing and compressive strength tests are shown in Table 3. For the linear traverse analysis, a slab was cut from each prism and one surface was polished and studied. The data on the void parameters are given in Table 4.

The compressive strength values on all batches were satisfactory. The mixtures utilizing SWR had the lowest w/c ratio and, as expected, attained the highest strength value. The non-air-entrained concrete with HPM had a w/c ratio higher than the control with an AEA, but yielded a higher compressive strength than the control because of the low air content obtained in the mixtures using HPM. As shown in Table 3, the durability factors (DF) of the specimens containing HPM 0.3 were much less than 60 and were unsatisfactory. The control attained a satisfactory DF. These results are in agreement with the linear traverse data, in which only the control showed a spacing factor less than 0.008 in. (0.2 mm). However, it should be noted that during polishing of the slab for the linear traverse analysis, it is possible to dislocate or destroy the HPM. Also, when an HPM is ruptured during the sample preparation, it could be invisible under the optical microscope. The high specific surface exhibited by the concrete containing fly ash may have resulted from the accidental inclusion of hollow fly ash particles as air bubbles.

Table 3

Results of Freezing and Thawing and Compressive Strength Tests
(Average of 4 Specimens)

Mixture No.	Variable	DF at 300 Cycles	WL in % at Time Test Ended	Cycles at which Test Ended	Compressive Strength at 28 days, psi
1	Control with AEA	79[a]	2.4[a]	290[a]	4,860
2	HPM 0.3	16	0.4	80	5,490
3	HPM 0.3 + SWR	34	0.0	173	7,100
4	HPM 0.3 + Fly Ash	15	0.4	74	4,900
5	Non-AE[a]	3	0.0	16	5,780
6	Non-AE with SWR[b]	8	0.0	40	7,070

[a]Average of 3 specimens

[b]Average of 2 specimens

Table 4

Air Void System of Hardened Mixtures Obtained by the
Linear Traverse Method

Mixture No.	Variable	Total Air, %	Specific Surface, in.$^{-1}$	$\bar{L}$, in.
1	Control with AEA	6.0	764	0.0059
2	HPM 0.3	1.4	565	0.0162
3	HPM 0.3 + SWR	3.1	272	0.0218
4	HPM 0.3 + Fly Ash	1.2	966	0.0099
5	Non-AE	1.0	219	0.0346
6	Non-AE with SWR	3.7	208	0.0264

NOTE: 1 in. = 25 mm.

SUBSEQUENT TEST PROGRAM

In the initial test program, the mixtures had a low dosage of HPM 0.3 and failed the freezing and thawing tests. However, these mixtures showed improvement over ordinary non-air-entrained concretes with or without SWR. Also, the results of tests reported by Mather indicated that satisfactory freeze and thaw resistance had been achieved in concrete to which HPM had inadvertently been added at a dosage of 4.1% by weight of cement.(5) Thus, a subsequent testing program was conducted in which varying dosages of HPM were utilized.

Materials

In the subsequent testing program, the fine aggregate used was a quartz sand with a specific gravity of 2.61 and a fineness modulus of 2.8. The coarse aggregate was a granite gneiss with a specific gravity of 2.78 and a dry rodded unit weight of 103.3 $lb./ft.^3$ (1650 kg/m^3). A chemical analysis of the Type II cement used in all the mixtures is given in the Appendix, which also includes the analysis of the fly ash used. Two types of super water reducers were used: the naphthalene type referred to in this report as SWRN and the melamine type referred to as SWRM.

Control and HPM Mixtures

Sample Preparation and Testing

The HPM was used in dosages of 0.3%, 1.5%, 3.0%, and 4.0% by weight of cement in non-air-entrained concretes. These dosages are referred to as HPM 0.3, HPM 1.5, HPM 3.0 and HPM 4.0, respectively. The volumes occupied at these dosages are 0.5%, 2.6%, 5.2%, and 7.0%, respectively, as calculated on the basis of a given density value. In addition to the voids created by HPM, there are the voids formed by entrapped air, which would yield total volumes of voids higher than the amounts stated above.

As controls, air-entrained mixtures were prepared with 3 levels of air entrainment and are denoted as control 1, control 2, and control 3. The mixture proportions for controls and the mixtures with HPM are given in Table 5. For the control mixtures there were 3 variables (three levels of air entrainment) and for the mixtures with HPM, 4 variables (4 levels of HPM dosage). The batches representing all variables were duplicated for assurance. The slump, air contents by pressure method ASTM C231 and the unit weights are given in Table 6. From each batch, three 3 x 4 x 16 in. (75 x 100 x 400 mm) beams, two for rapid freezing and thawing tests and one for linear traverse analysis, and two 6 x 12 in. (150 x 300 mm) cylinders for compressive strength determinations were made.

Table 5

Mixture Proportions for Control and HPM Mixtures by Weight Relative to Cement

INGREDIENT	CONTROL			HPM, Percent by Weight of Cement			
	1	2	3	0.3	1.5	3.0	4.0
Cement*	1	1	1	1	1	1	1
w/c	0.51	0.49	0.47	0.51	0.49	0.47	0.45
C.A.	3.18	3.18	3.18	3.18	3.18	3.18	3.18
F.A.	2.18	2.08	1.99	2.18	2.08	1.99	1.89

*Cement = 588 lb./yd.^{3} = 349 kg/m^3.

Table 6

Properties of Plastic Concrete in Control and HPM Mixtures

Variable	Batch	Slump, in.	C231 Air, %	HMS, %*	Unit Weight, lb./ft.^{3}
Control 1	1	3.6	4.0	---	148.8
Control 1	2	2.2	3.8	---	149.6
Control 2	1	3.0	4.6	---	150.0
Control 2	2	2.9	4.9	---	149.2
Control 3	1	3.7	8.4	---	145.2
Control 3	2	3.0	6.4	---	147.6
HPM 0.3	1	2.0	2.5	0.3	151.2
HPM 0.3	2	1.8	2.8	0.3	151.2
HPM 1.5	1	3.2	2.8	1.5	149.4
HPM 1.5	2	2.5	3.6	1.5	149.0
HPM 3.0	1	3.0	3.3	3.0	147.6
HPM 3.0	2	2.5	4.4	3.0	146.6
HPM 4.0	1	2.6	4.2	4.0	145.8
HPM 4.0	2	2.4	4.5	4.0	145.2

NOTE: 1 in. = 25 mm; 1 lb./ft.^{3} = 16 kg/m^3.

*By weight of cement.

Results

The results of the freeze-thaw tests are summarized in Table 7, which also gives the total air contents determined at the fresh and hardened stages. These results indicate that control 1 had an unacceptable weight loss, WL, durability factor, DF, and surface rating, SR. Control 2 had a satisfactory DF, but unsatisfactory WL and SR. The air content for control 2 at the hardened stage was 4.4%. Control 3, with an air content of 7.4%, exhibited satisfactory performance in terms of the WL, DF, and SR. HPM 0.3 failed the acceptance criteria. HPM 1.5, HPM 3.0, and HPM 4.0 had satisfactory resistance to damage from cycles of freezing and thawing. Thus, HPM used in dosages of 1.5% by weight of cement or more provided satisfactory freeze-thaw resistance. Figures 1 and 2 show the relationship between the air content or HPM dosage and the DF. The linear traverse data in Table 8 indicate that of the controls, only control 3 had an $\bar{L}$ value less than the 0.008 in. (0.20 mm) required for satisfactory freeze-thaw durability, which is consistent with results of the rapid freeze-thaw tests. All the samples with HPM had $\bar{L}$ values above 0.008 in. (0.20 mm), even though most of the mixtures exhibited satisfactory freeze-thaw resistance. However, it should be noted that it is difficult to observe hollow plastic microspheres under the microscope as needed during the linear traverse analysis, because of the small size of HPM and because they were lost or became invisible when punctured during the preparation of the samples, which involved cutting and polishing.

The compressive strengths given in Table 9 indicate satisfactory strength levels and, generally, that the increase in air or HPM led to lower strength values.

Table 7

Freeze-thaw Data at 300 Cycles for Control and HPM Mixtures as an Average of 4 Beams

Variable	C231 Air, %	C457 Air, %	Cycles at Which Test Ended	WL Loss, %	DF	SR
Control 1	3.9	3.7	72	25.0	15	5.0
Control 2	4.8	4.4	300	14.0	81	3.9
Control 3	7.4	7.4	300	3.7	100	2.0
HPM 0.3	2.7	2.9	77	2.5	16	5.0
HPM 1.5	3.2	3.2	300	4.5	81	2.6
HPM 3.0	3.9	4.5	300	2.7	96	2.1
HPM 4.0	4.3	3.4	300	2.3	95	2.2

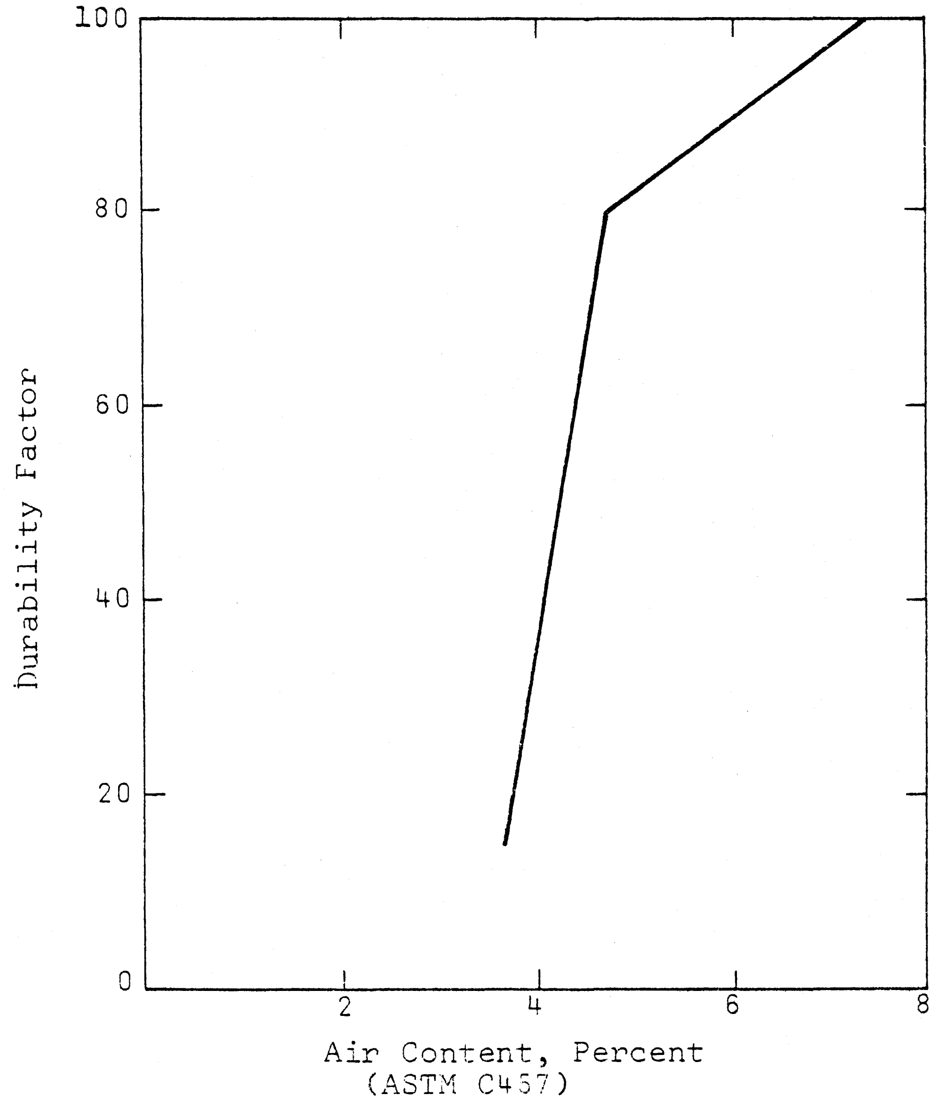

Figure 1. Air content versus durability factor in control mixtures.

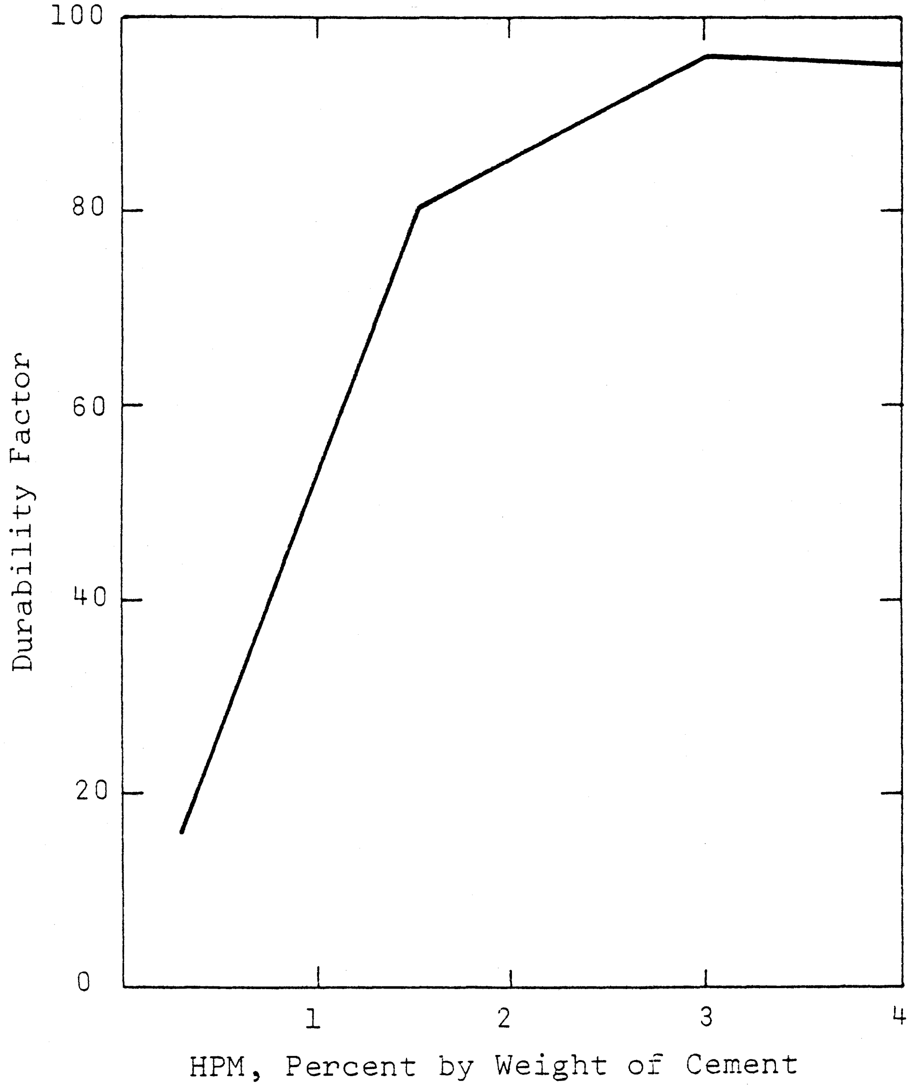

Figure 2. HPM content versus durability factor in non-air-entrained mixtures with HPM only.

Table 8

Linear Traverse Data for the Control and the HPM Mixtures

Variable	< 1 mm	>1 mm	Air, %	Specific Surface, in.$^{-1}$	$\bar{L}$, in.
Control 1	2.1	1.6	3.7	240	0.0235
Control 2	3.2	1.2	4.4	328	0.0157
Control 3	5.6	1.7	7.3	474	0.0077
HPM 0.3	2.1	0.8	2.9	273	0.0233
HPM 1.5	2.6	0.6	3.2	384	0.0154
HPM 3.0	3.4	1.1	4.5	498	0.0101
HPM 4.0	2.5	0.9	3.4	476	0.0118

NOTE: 1 in. = 25 mm.

Table 9

28-Day Compressive Strengths in PSI for the Control and the HPM Mixtures as an Average of 4 Samples

Variable	Average	Std. Dev.
Control 1	5,360	73
Control 2	5,430	119
Control 3	4,970	190
HPM 0.3	5,480	294
HPM 1.5	4.960	164
HPM 3.0	4,220	90
HPM 4.0	3,910	99

NOTE: 1 psi - 6.89 kPa.

HPM Mixtures with SWR and Fly Ash

Sample Preparation and Testing

The HPM dosage found to provide satisfactory freeze-thaw resistance, 1.5% by weight of cement, and twice this dosage were used in non-air-entrained mixtures containing SWR and fly ash. The mixture proportions are given in Table 10. The two types of SWR used are referred to as SWRN and SWRM. SWRN was a 42% solids solution of naphthalene sulfonate polymer, which was added at a dosage of 1.2% by weight of cement. SWRM was a 20% solids solution of melamine sulfonate polymer and was added at a dosage of 3.3% by weight of cement. In these mixtures about 20% reductionsin water content of regular control or HPM mixtures were used. Also, one other set of mixtures were prepared using SWRN at a dosage of 0.6% by weight of cement with the same amount of water used in control or HPM mixtures. This concrete was referred to as flowing, F, concrete. In the fly ash mixtures a 17% reduction by weight in the cement content of regular batches was made.

All batches were prepared using the standard mixing procedure which consists of adding all ingredients to the mixer; mixing for 3 minutes, waiting 3 minutes, and mixing for 2 minutes. The SWR admixture was added to the batches at the beginning of the final 2 minutes of mixing. Following the completion of the mixing the concrete was tested for slump, air content ASTM C231, and unit weight. The results of these measurements are shown in Table 11. In this test program the same number of specimens as in the control mixtures were prepared, except in the linear traverse analysis only one slab for each variable was tested.

Table 10

Mixture Proportions for Concrete with SWR and Fly Ash by Weight Relative to Cement

Ingredient	Kleenopor, (Percent by weight of cement)				
	1.5	3.0	1.5	1.5	3.0
Cement	1*	1*	1*	1**	1**
Water	0.39	0.38	0.49	0.59	0.57
Coarse Agg.	3.18	3.18	3.18	3.83	3.83
Fine Agg.	2.33	2.23	2.08	2.38	2.27
Fly Ash	--	--	--	0.27	0.27

*Mixtures containing SWR, cement = 588 lb./yd.^{3} = 349 kg/m^3.

**Cement = 488 lb./yd.^{3} = 290 kg/m^3.

Table 11

Properties of Plastic Concrete in Mixtures with
SWR and Fly Ash

Variable	Batch	Slump, in.	C231 Air, %	HPM, %*	Unit Weight, lb./ft.^{3}
SWRN + HPM 1.5	1	2.7	3.8	1.5	151.6
SWRN + HPM 1.5	2	2.8	3.2	1.5	151.0
SWRN + HPM 3.0	1	3.1	4.3	3.0	150.2
SWRN + HPM 3.0	2	2.0	4.6	3.0	150.0
SWRNF + HPM 1.5	1	6.5	3.1	1.5	150.0
SWRNF + HPM 1.5	2	8.0	2.6	1.5	151.2
SWRM + HPM 1.5	1	6.0	2.5	1.5	152.4
SWRM + HPM 1.5	2	5.3	3.0	1.5	151.2
SWRM + HPM 3.0	1	2.5	3.7	3.0	149.8
SWRM + HPM 3.0	2	4.0	3.6	3.0	150.0
Fly Ash + HPM 1.5	1	3.2	3.3	1.5	148.0
Fly Ash + HPM 1.5	2	1.9	3.2	1.5	149.2
Fly Ash + HPM 3.0	1	3.8	4.8	3.0	144.6
Fly Ash + HPM 3.0	2	3.5	4.5	3.0	145.2

NOTE: 1 in. = 25 mm; 1 lb./ft.^{3} = 16 kg/m^3.

*By weight of cement.

Results

The flowing concrete obtained by adding SWR to a non-air-entrained concrete with HPM yielded high slump values as expected. The freeze-thaw data in Table 12 indicate that all the mixtures containing SWR and HPM at dosages of both 1.5% and 3.0% failed to exhibit satisfactory freeze-thaw resistance since they all had low DF values. However, there were improvements in the DF as the HPM dosage was increased, as can be seen in Table 12 or Figure 3. Mixtures with fly ash exhibited desirable DF values at both dosages and higher values were achieved with a larger HPM dosage, as shown in Figure 3. However, at an HPM dosage of 1.5%, the fly ash concretes displayed an unacceptable level of WL, indicating a higher rate of scaling of fly ash mixtures as compared to the regular concretes. The linear traverse data are summarized in Table 13, where it can be seen that all the spacing factors were higher than 0.008 in. (0.20 mm), except that for the mixture with fly ash and HPM at 3.0%.

Table 12

Freeze-thaw Data for Mixtures with SWR and Fly Ash as an Average of 4 Beams at 300 Cycles

Variable	C231 Air, %	C457 Air, %	Cycles at Which Test Ended	WL, %	DF	SR
SWRN + HPM 1.5	3.5	3.3	128	8.9	26	3.5
SWRN + HPM 3.0	4.5	4.4	215	4.0	43	2.1
SWRNF + HPM 1.5	2.8	1.7	124	22.0	25	5.0
SWRM + HPM 1.5	2.8	2.4	86	14.0	17	5.0
SWRM + HPM 3.0	3.6	2.7	186	4.5	37	2.2
Fly Ash + HPM 1.5	3.2	4.2	300	11.6	80	4.0
Fly Ash + HPM 3.0	4.7	2.9	300	6.0	91	3.1

The difficulties encountered in analyzing the mixtures with HPM and the possibility of taking hollow fly ash particles as air voids could explain the very high specific surface value for the fly ash mixture with HPM 3.0.

The compressive strengths in Table 14 indicate that the use of SWR provides an increase in compressive strength, which is as would be expected based on the reduction in the w/c achieved. The mixtures with fly ash and HPM exhibited lower compressive strengths at 28 days than did the counterparts with HPM only, which displayed the slower strength gain characteristic of fly ash concretes.

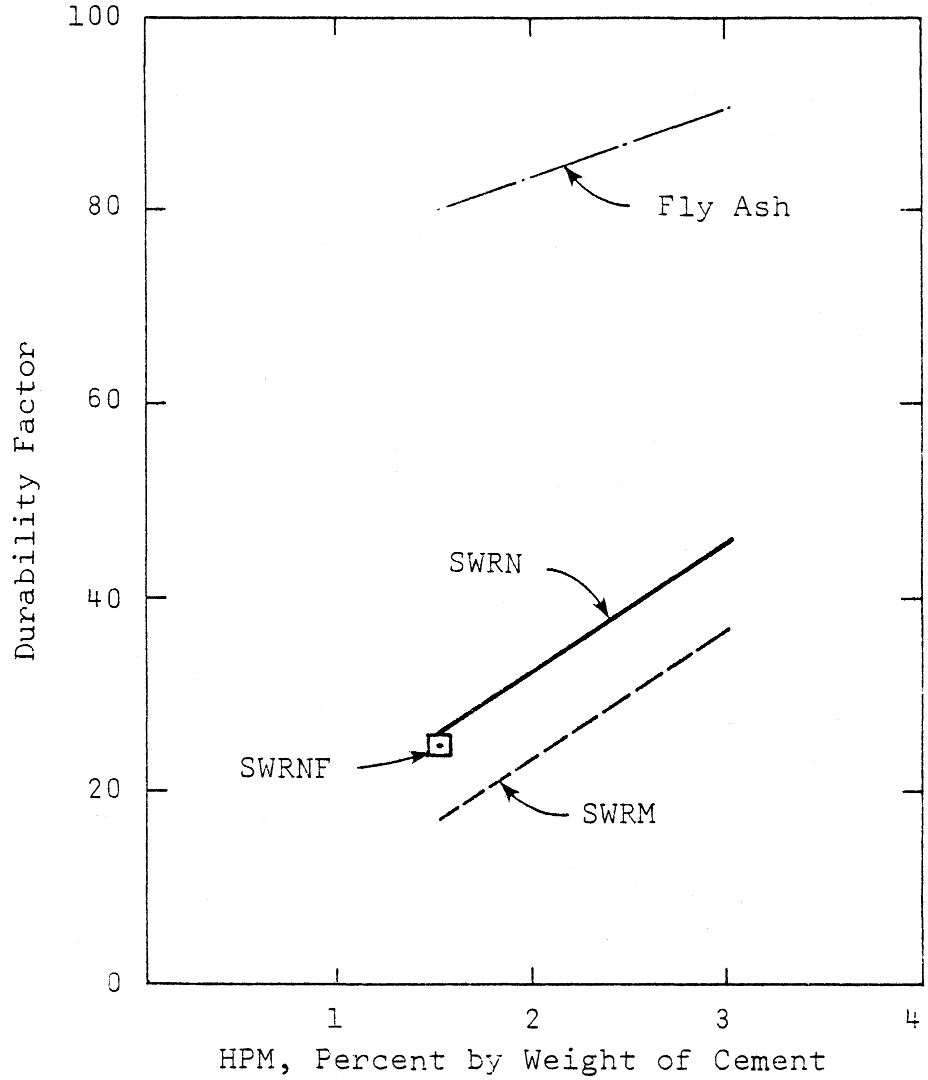

Figure 3. HPM content versus durability factor for non-air-entrained HPM mixtures with super water reducers or fly ash.

Table 13

Linear Traverse Data for the Mixtures with
SWR AND HPM

Variable	<1 mm	>1 mm	Air, %	Specific Surface, in.$^{-1}$	Spacing Factor, in.
SWRN + HPM 1.5	2.2	1.1	3.3	207	0.0279
SWRN + HPM 3.0	2.4	2.0	4.4	326	0.0157
SWRNF + HPM 1.5	1.5	0.3	1.7	454	0.0171
SWRM + HPM 1.5	1.2	1.2	2.4	249	0.0268
SWRM + HPM 3.0	1.9	0.8	2.7	292	0.0219
Fly Ash + HPM 1.5	2.9	1.3	4.2	347	0.0149
Fly Ash + HPM 3.0	2.2	0.7	2.9	1,105	0.0056

NOTE: 1 in. = 25 mm.

Table 14

28-Day Compressive Strengths in PSI for the Mixtures with
SWR and Fly Ash as an Average of 4 Samples

Variable	Average	Std. Dev.
SWRN + HPM 1.5	6,300	211
SWRN + HPM 3.0	5,980	84
SWRM + HPM 1.5	6,060	174
SWRM + HPM 3.0	6,090	205
SWRNF + HPM 1.5	4,720	200
Fly Ash + HPM 1.5	4,670	376
Fly Ash + HPM 3.0	3,590	220

NOTE: 1 psi = 6.89 kPa

Microscopic Studies

To determine the cause of the low durability in the concretes with HPM and SWR, microscopic studies were conducted using an optical microscope and a scanning electron microscope as explained below.

Optical Microscope

After careful examination of the samples with HPM and those with HPM and SWR under the Research Council's optical microscope, certain trends were noted. More HPM microspheres were observed in mixtures with HPM only compared to those with HPM and SWR, even though the same dosages of HPM were used. At the surface of entrapped air voids of the specimens from the HPM only mixtures, which are larger than the microspheres, numerous HPM voids were noticed, whereas in the mixtures with HPM and SWR the walls of the entrapped air voids were free of the microspheres. In the mixtures with HPM and SWR, Figure 4, an accumulation of HPM under the aggregate (white deposit) was noticed, whereas none was observed in mixtures with HPM only, as shown in Figure 5.

The information gained with the optical microscope was limited; only trends could be observed and definite conclusions could not be drawn. The magnification was limited to about 100X and polishing the samples caused the HPM to disappear or become invisible when punctured. Because of these limitations a further limited study was conducted using the scanning electron microscope.

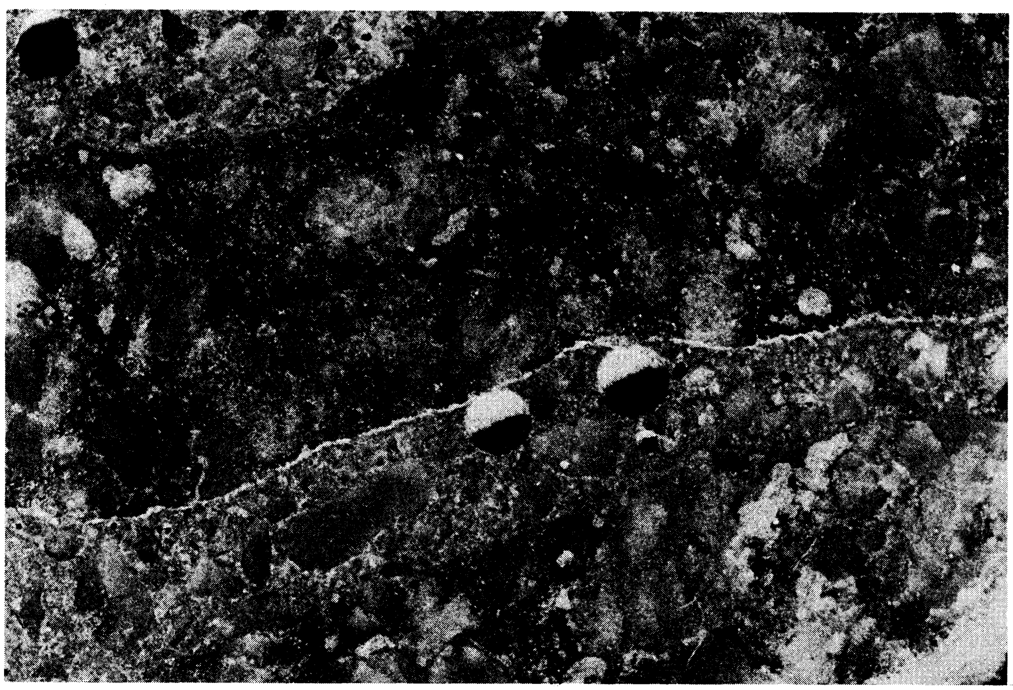

Figure 4. Photomicrograph of a mixture containing HPM and SWR. Accumulation of HPM (white residue running from upper right center to lower left) under the aggregate is noted. (8X)

Figure 5. Photomicrograph of a mixture containing HPM. No visible accumulation of HPM under the aggregate. (8X)

Scanning Electron Microscope (SEM)

With the SEM, higher magnifications than are possible with the optical microscope can be utilized. Also, fractured specimens are used rather than the polished ones.

The SEM equipment of the University of Virginia's Materials Science Department was used and samples were prepared from a control mixture, mixtures with HPM at dosages of 1.5% and 3.0%, and mixtures with SWR and HPM at the same dosages as used in the HPM only mixtures.

Some of the SEM micrographs taken are shown in Figures 6-11. Figure 6 shows an air void, taken at 300X magnification, exhibiting a smooth surface and reaction products. Figure 7 is a micrograph of mixture with HPM well distributed; numerous HPM voids are observed at 30X magnification. At 300X magnification, Figure 8, the HPM particles are enlarged and the plastic surface coating is visible. The roughness of the HPM surface is noticed. Figure 9 shows the mixtures with SWR and HPM at 30X. The HPM are fewer than in Figure 7, even though both mixtures had the same amount of HPM.

Figure 6. SEM micrograph of an air void with smooth surface and reaction products.(300X)

Figure 7. SEM micrograph of a mixture with HPM at a dosage of 3.0% by weight of cement. (30X).

Figure 8. SEM micrograph of a mixture with HPM at a dosage of 3.0% by weight of cement. (300X)

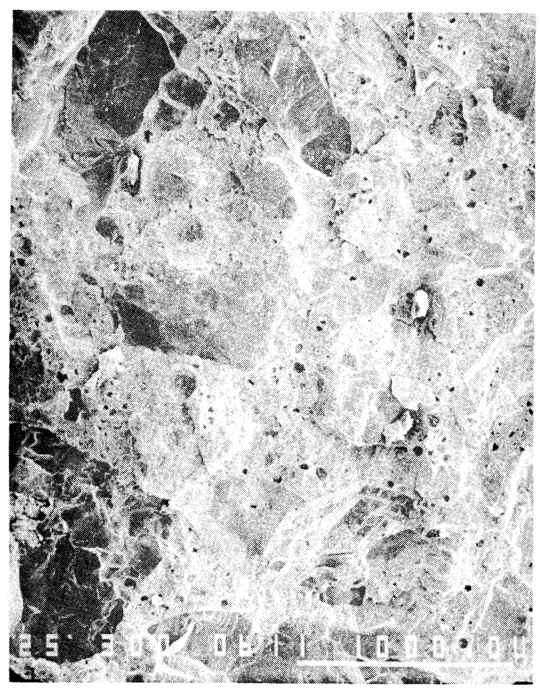

Figure 9. SEM micrograph of a mixture with SWR and HPM at a dosage of 3.0% by weight of cement. (30X)

Figure 10. SEM micrograph of a mixture with SWR and HPM at a dosage of 3.0% by weight of cement. (300X)

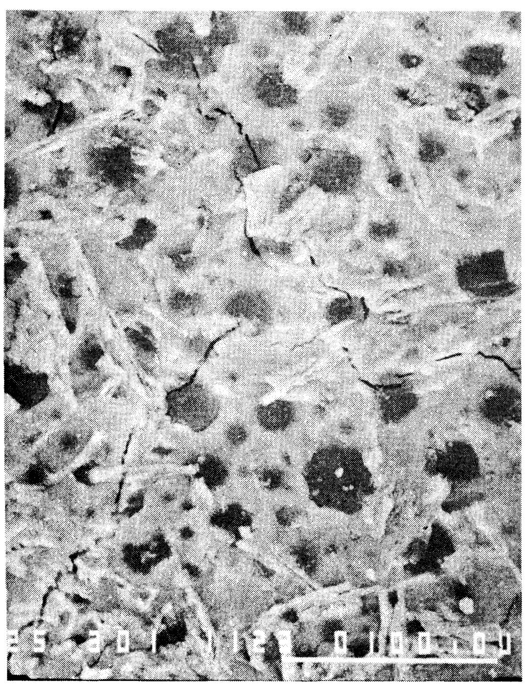

Figure 11. SEM micrograph showing the bottom of an air void in a mixture with HPM. (300X)

Figure 10 is an SEM micrograph of the mixture with SWR and HPM at 300X. An air void is visible at the top left corner and there also are a few HPM voids filled with calcium. The air void has smooth sides and does not contain HPM voids. Figure 11 shows the bottom of an air void in an HPM only mixture and the HPM voids are visible. Thus, the trends observed with the optical microscope were confirmed by the SEM investigation.

It is believed that SWR's are surface-active agents that charge cement particles and cause them to repel each other.(6) The repelling action probably provides internal agitation in the concrete mixture, which in turn probably causes the HPM to move upward due to their low densities. Consequently these HPM are trapped on the bottom surface of the aggregates, while others probably escape to the surface of the concrete mixture. Because the ones that are lost to the surface or trapped under the aggregate do not contribute to frost resistance, larger quantities of HPM are required to protect concrete containing SWR than concrete that does not.

Furthermore, in conventional concrete the HPM collect in large entrapped air voids, whereas in SWR concrete they are probably dispersed under the influence of the surface-active agent. Because the large entrapped air voids are so few in number, an accumulation or the lack of HPM in the voids has little influence on the frost resistance of the concrete; more importantly, the presence or lack helps to explain the behavior of the HPM in concrete that contains SWR as compared with ones that don't.

CONCLUSIONS

1. The use of HPM in non-air-entrained concrete improves its resistance to damage from cycles of freezing and thawing. At the lowest dosage of 0.3% HPM by weight of cement used in this study, the resistance provided was inadequate as tested by ASTM C666 procedure A. However, at the second low dosage of 1.5% and above, the concretes attained satisfactory freeze-thaw durability.

2. Hardened control concretes with an air content of 3.7% displayed inadequate freeze-thaw durability. Controls with 4.4% exhibited satisfactory internal durability, but excessive, unacceptable surface scaling. The hardened control mixture with a content of 7.3% had satisfactory freeze-thaw durability.

3. Mixtures incorporating SWR and HPM at dosages of 1.5% and 3.0% exhibited unacceptable freeze-thaw resistance.

4. Concretes with fly ash and 1.5% and 3.0% HPM had satisfactory internal durability. At the lower dosage, however, high surface scaling was noticed.

5. In mixtures with only HPM, the HPM were well distributed and numerous HPM voids were noticed. The paste of mixtures with the same dosage of HPM and also with SWR contained few HPM and the HPM were poorly distributed. Also in these concretes, concentrations of HPM at the underside of the aggregate were observed, which indicated an upward movement of HPM in the concrete.

6. Sample preparation for the examination with an optical microscope damaged or destroyed some of the HPM. The small size of the HPM made it difficult to observe them with an optical microscope at a magnification of 100X.

7. The scanning electron microscope (SEM) provided a good picture of the fractured concrete surfaces and confirmed the trends observed with the optical microscope.

RECOMMENDATION

At this time, hollow plastic microspheres are not recommended for use in concrete as a means for providing resistance to damage from cycles of freezing and thawing. Tests to date show that although the desired durability is obtained in regular concrete at certain dosages, the costs for adequate protection would be very high. Based upon information supplied by the producer at the initiation of this study, the use of hollow plastic microspheres in bridge deck concretes would cost about \$19/yd.^{3} (\$25/m^3). However, air-entraining admixtures for the same quantity of concrete would be less than a quarter, or approximately 1% the cost of the microspheres. In addition, adequate protection is not provided by the microspheres in normal amounts when used in concrete containing super water reducers.

ACKNOWLEDGEMENTS

Special thanks are expressed to L. Th. Metz of Akzo Chemie for furnishing the hollow plastic microspheres used in this study. Also special thanks go to Dr. W. Jesser and R. Ladd of the University of Virginia's Materials Science Lab for the SEM work, and to Hollis Walker for the petrographic examinations. Appreciation is expressed to Clyde Giannini, Bobby Marshall, Mike Burton, and Sallie Miller for the preparation and testing of the specimens.

REFERENCES

1. Halstead, W. J., "Quality Control of Highway Concrete Containing Fly Ash", VHTRC 81-R38, Virginia Highway and Transportation Research Council, Charlottesville, Virginia, February 1981.

2. "Control of Entrained Air in Concrete", Brief of NCHRP Research Problem Statement Considered by the Special AASHTO Select Committee on Research for FY 1981, August 1979.

3. Kaper, L., "New Methods for the Improvement of the Frost and Deicing Salt Resistance of Concrete", Amersfoort, Holland, September 1977.

4. Mielenz, R. C., V. E. Wolkodoff, J. E. Backstrom, and R. W. Burrows, "Origin, Evolution, and Effects of the Air Void System in Concrete, Part 4 — The Air Void System in Job Concrete", ACI Journal, October 1958.

5. Mather, Bryant, "Summary of Freezing and Thawing Tests of Kleenopor", Waterways Experiment Station, Vicksburg, Mississippi, January 1979.

6. "Superplasticizing Admixtures in Concrete", Cement and Concrete Association, Waxham, Springs, Slough, January 1976.

APPENDIX

Cement & Fly Ash Analyses

FLY ASH

Form TL-47 Rev. 6-74

VIRGINIA DEPARTMENT OF HIGHWAYS AND TRANSPORTATION
MATERIALS DIVISION

REPORT ON SAMPLE OF MISCELLANEOUS MATERIAL

Route No. Investigation

Project No.

F. H. W. A. No.

County

Order No.

Sample No.

Laboratory No. MS 58827 Richmond, Va., 2-4, 1980

Material Fly Ash Quantity

Tested for conformity with specifications for

Manufactured By

Submitted By Ferron At Charlottesville Research Council

For District Engineer, Va.

On ,19 Received ,19

Consigned To

$SiO_2 + Al_2O_3 + Fe_2O_3$	=	93.1 %	Blaine = 3110
SiO_2	=	53.1 %	Cm^2/Cm^3 = 7090
Al_2O_3	=	35.7 %	Sp. Gr. = 2.28
Fe_2O_3	=	4.3 %	
MgO	=	.65 %	
SO_3	=	1.3 %	
Available Alkali	=	0.56 %	
Na_2O =		0.21 %	
.658 x K_2O =		0.35 %	
Ignition Loss	=	1.51 %	
Moisture	=	0.14 %	

Reported As

By

Date 2-5-80

1 - R.Steele

Code No.

Insp. Test Cost

Debit Memo No.

By [signature]
State Materials Engineer

LONE STAR CEMENT INC.

MILL LABORATORY TESTS

Roanoke, Va. Plant

ıpped To:
.dress:

Reported To: Virginia Highway & Transportation Research Council
Address: P. O. Box 3817
University Station
Charlottesville, Va. 24903
Attn: Clyde Giannini

te Shipped	Car or Truck No.	Type Cement	Tons	Silo No.
		II	15 bags	

TEST DATA ON STOCK FROM WHICH SHIPMENT WAS MADE

CHEMICAL	SILO NO.			
$)_2$	21.5			
$:O_3$	4.6			
O_3	4.0			
Ͻ	63.0			
O	2.8			
$_3$	2.4			
tal Alkalies	.78			
oluble Residue	-			
ition Loss	-			
:ential Comp.				
C_3S	50			
C_3A	5			

PHYSICAL	SILO NO.			
Fineness — Blaine	3143			
— Wagner	1896			
Autoclave Expansion	.037			
Initial Set (Hr., Min.)	3:45			
Final Set (Hr., Min.)	6;00			
Vicat (Min.)	190			
Air Content of Mortar	8.9			
Tensile Strength (psi)				
1 Day				
3 Day				
7 Day				
28 Day				
Compressive Strength (psi) 1 Day	1583			
3 Day	2600			
7 Day				
28 Day				

is will certify that the cement in the shipments listed above complies with
TM Specification C-150-78, Federal Specification SS-C-1960,
.SHO Specification M-85-75, and/or ,

ATE OF Virginia
)UNTY OF Botetourt

R. J. Johnson, Being duly sworn deposes and says: That he is
emist-Analyst of LONE STAR CEMENT INC. who prepared the above report of tests and that the same is true and correct.

R. J. Johnson

›scribed and sworn to before me this
1th day of September, 19 79.

Patricia C. Ellis
Notary Public

Commission expires 4-22-80

103