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Freezing and Thawing of Concrete and Use of Silicones

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Silicones as Admixtures for Concrete

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• A RECENT report of the Bureau of Public Roads (1) showed that given amounts of a certain silicone as an admixture for concrete were effective in preventing scaling caused by de-icing agents. This silicone also increased the compressive strength of the concrete but caused a marked retardation in the setting of the concrete. Because of these effects, additional tests were made to determine if other silicones used as admixtures would give similar results.

In these latter tests, eight different silicones manufactured by the three major producers were used. Tests were made to determine the effect of silicone admixtures on the properties of fresh concrete and on the strength and durability of hardened concrete. Tests using some of the silicones were limited due to insufficient quantities of the silicone samples.

MATERIALS

The tests were made on air-entrained concrete prepared with varying amounts of eight different silicone solutions. The physical and chemical properties of these silicone solutions are given in Table 1. The silicones are grouped into three general classes. Four of them (silicones A, B, C, and D) are classified as sodium methylsiliconates, two (silicones E and F) are classified as alkyl silane esters, and two (silicones G and H) as silicone resin emulsions. Typical infrared spectra of the silicones are shown in Figure 1. All silicones in each group show the same general characteristic spectra. With the exception of the two emulsions (silicones G and H), which were milky white liquids, all were colorless liquids. The solvent or thinner for six of the silicones (A, B, C, D, G, and H) was water; for the other two (E and F), it was an alcohol.

Except for the silicone admixtures, the same concrete materials were used for all of the tests. The cement was a Type I portland cement with an equivalent alkali content of 0.6 percent. The chemical analysis of the cement is given in Table 2. The aggregates were similar to those used in the previous investigation of a silicone as an admixture. These were a siliceous sand having a fineness modulus of 2.75 and a uniformly-graded crushed limestone of 1-in. maximum size. A commercially available aqueous solution of neutralized Vinsol resin was used to entrain air.

MIX DATA

The mix data for the concretes are given in Table 3. The concrete contained 6 bags of cement per cubic yard, the air content was approximately 5 percent, and the slump was about 3 in. A control or reference mix without silicone was made on each day, and the mixes containing silicone were compared to the corresponding control mix made on the same day. The average values for all the control mixes are given in footnote 1 of the table.

The total solids in the silicone solutions added to the mixes varied from 0.01 to 1.33 percent by weight of the cement. The concentration of the total solids in the eight silicone solutions varied. From literature furnished by the producers, the approximate percentage of total solids in each solution was assumed for convenience in designing the mixes. These values are given in footnote 1 of Table 3.

The actual percentage of total solids in six of the eight solutions was determined chemically (Table 1). These values were within five percentage points of those used.

Paper sponsored by Committee on Chemical Additions and Admixtures for Cement.

TABLE 1

PHYSICAL AND CHEMICAL PROPERTIES OF SILICONE SOLUTIONS

Property	Sodium Methylsiliconate (sodium salt of methyl poly-siloxane)				Alkyl Silane Ester		Silicone Resin Emulsion of R-23 Silicone Resin	
					Methyl Chloro-silane "M"	Ethyltri-Ethoxysilane	Nonionic Type, G	Anionic Type, H
	A	B	C	D	E	F		
pH (electrometric method)	12.1	12.0	12.2	12+	2.6	7.2	7.2	8.4
Specific gravity 25 C/4 C	1.244	1.252	1.102	1.227	0.952	0.901	1.027	1.008
Chemical analysis:								
Total solids (non-vol. at 150 C, 90 min) (%)	33.5	33.3	33.1	30.1	---[2]	---[2]	41.4	16.9
Total sodium as Na_2O (%)	10.4	10.3	11.2	12.4	---	---	---	---
Silicon (%)	8.2	8.1	8.5	5.6	21.7	3.8	8.9	3.4
Chlorine (%)	---	---	---	---	None[3]	---	---	---
Silicone solids as $CH_3SiO_{1.5}$ (%)	19.6	19.4	20.3	13.4	---	---	---	---
Molecular ratio ($CH_3SiO_{1.5}/Na_2O$)	1.7	1.7	1.7	1.0	---	---	---	---
Infrared analysis of active constituent	All four materials found similar, showed methylsiliconate structure; D had more sodium carbonate impurity than others.				Spectra of both materials fairly similar, showing alkyl silane ester structure; F showed ethyl groups, E showed mostly methyl substitution.		Both materials showed similar spectra of presumably condensed silicones with ethyl substitution.	
Infrared analysis of vol. solvent or thinner					Both solvents appear alcohol type, but exact identification difficult because of some volatility of active constituent.			
Probable formula	$[CH_3Si(OH)_2O]\ Na^+$ [4] $[CH_3SiO_2Na]_n$ [5]				$(CH_3)_nSi(OCH_3)_{4n}$	$C_2H_5Si(OC_2H_5)_3$	$[R''O(R'_x)SiO_{\frac{4-x}{2}}]_nR'$	

---

[1] Description.

[2] Not determined because of volatility of silicone material.

[3] Qualitative test.

[4] In dilute aqueous solution.

[5] In dry form.

for designing the mixes. For silicones E and F (the alkyl silane esters), it was impossible to determine the amount of total solids because of the volatility of the silicone materials.

For six of the silicones (A, B, C, D, E, and F), the assumed concentration of the solutions was 30 percent total solids. For this concentration, 10 oz of the solution per bag of cement is equivalent to 0.2 percent total solids by weight of cement. In Table 3, the amount of the silicone solution used in each mix is given as the weight of total solids in the quantity of solution used expressed as a percentage of the weight of cement. It is also given as the number of ounces of the solutions per bag of cement.

Mixing and Curing

The mixing and curing was in accordance with standard laboratory procedures. The aqueous solution of each silicone was added with part of the mixing water to the cement and aggregates in the mixer before the addition of the aqueous solution of the air-entraining admixture.

ASTM standard methods were followed in making tests on the plastic concrete and in molding, curing, and testing the specimens of hardened concrete. The tests for outdoor scaling were made as described in an earlier report (1).

Water and Air Content

Data on the effect of silicones as admixtures on the water and air content of concrete are shown in Table 3 and Figure 2. The figure shows that concretes with the silicone admixtures generally needed less water for the same slump than reference concretes prepared on the same days. However, in most cases, the reduction in water was 3 percent or less.

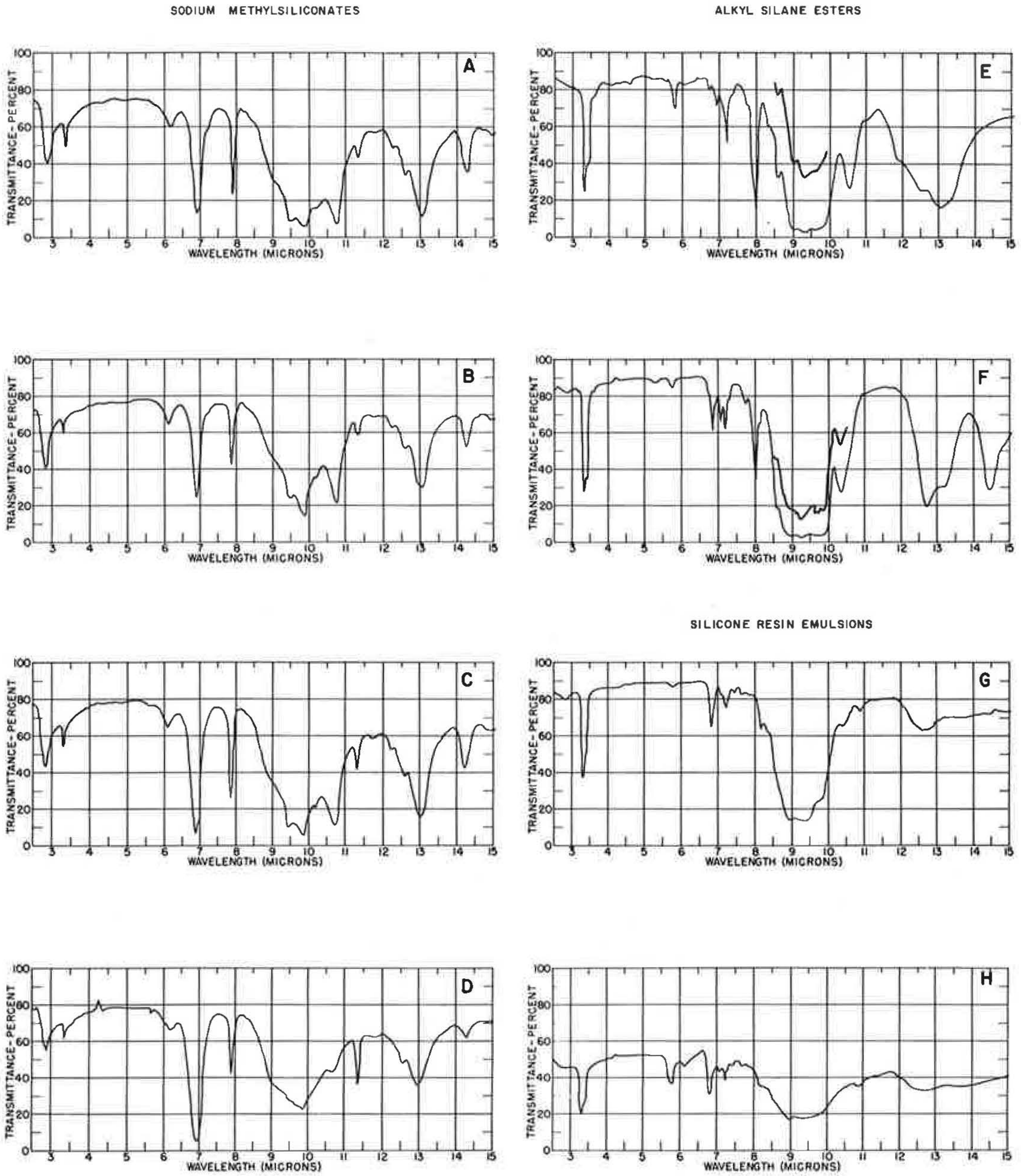

Figure 1. Infrared spectra of silicone admixtures.

In 9 of the 11 mixes showing a reduction in water of more than 3 percent, more than 10 oz of the silicone solution per bag of cement (0.2% total solids by weight of cement) was used. The data for reduction in amount of mixing water are erratic for some of the silicones. Due to time and mold limitations, not all the mixes prepared with the different amount of any one silicone were made on the same day, and they were therefore compared with a different control mix. This would account for some of the erratic results. For silicones B and E, except for one mix for each, a progressive reduction in mixing water was found with increases in the amount of the silicone. Silicone H also

TABLE 2

PHYSICAL AND CHEMICAL PROPERTIES OF PORTLAND CEMENT

Property	Value
Chemical composition (%):	
Silicone dioxide	20.9
Aluminum oxide	6.0
Ferric oxide	2.5
Calcium oxide	65.3
Magnesium oxide	1.4
Sulfur trioxide	2.2
Loss on ignition	0.7
Insoluble residue	0.19
Sodium oxide	0.14
Potassium oxide	0.75
Chloroform soluble	0.007
Free lime	0.76
Equiv. alkali as Na_2O	0.63
Computed compound composition (%):	
Tricalcium silicate	57
Dicalcium silicate	17
Tricalcium aluminate	12
Apparent specific gravity	3.14
Specific surface (Blaine) (Cm^2/g)	3,250
Autoclave expansion (%)	0.05
Normal consistency	24.2
Time of setting (Gillmore test) (hr):	
Initial	4.25
Final	6.83
Compressive strength (1:2.75 mortar) (psi):	
3 days	2,850
7 days	3,830
28 days	5,170
Mortar air content (%)	9.4

caused a reduction in the mixing water when silicone solids of 0.5 percent or more were used. Silicones C and F reduced the mixing water requirement until about 0.5 percent silicone solids were used, but when greater amounts were used, more water was required.

Although the general trend is for greater reductions in the water required with increases in the amount of silicone used, these data fail to show that the silicones used are effective water-reducing agents.

The use of silicones as admixtures had some effect on the air content of the concrete. Table 3 gives the amount of air-entraining agent needed in the mixes prepared with the silicone admixtures as a percentage of the amount of agent needed in the control concrete made on the same day. This is also shown in the upper portion of Figure 3. In general mixes prepared with less than 0.2 percent total silicone solids, less air-entraining agent was needed than in the control mix. However, for mixes prepared with larger amounts of the silicones, more air-entraining agent was required than for the control mix. For silicone D, more air-entraining agent was required for all mixes except one.

When silicone E was used, the concrete expanded during the hardening process. With the largest amount of silicone E (0.5% solids by weight of cement) the concrete expanded 1 in. above the top of the 6- by 12-in. cylinder molds. The air content of this plastic concrete, determined immediately after mixing, was 4.5 percent. The unit weight of the hardened concrete for each of the mixes prepared with silicone E was determined on the cylinders before testing for compressive strength. These weights are given in Table 3 and the lower portion of Figure 3. The weight of the control concrete was 149.1 pcf, whereas the weight of the concrete prepared with 0.5 percent silicone solids was only 135.9 pcf. As the weights of the two plastic concretes immediately after mixing were nearly the same, this shows that the concrete containing 0.5 percent silicone solids expanded about 10 percent.

Tests were made to determine the cause of the expansion of the concrete prepared with silicone E. It was found that when this silicone solution is treated with saturated limewater, it hydrolyzes and produces a mixture of alcohol containing perhaps both methyl and ethyl types. Inasmuch as the parent silicone is an ester, such hydrolysis would be expected. The same result could be expected when the material is added to concrete, where lime is immediately produced as a result of reaction of cement with mixing water. If the alcohols are produced in a gaseous form, this would account for the foaming (swelling) observed.

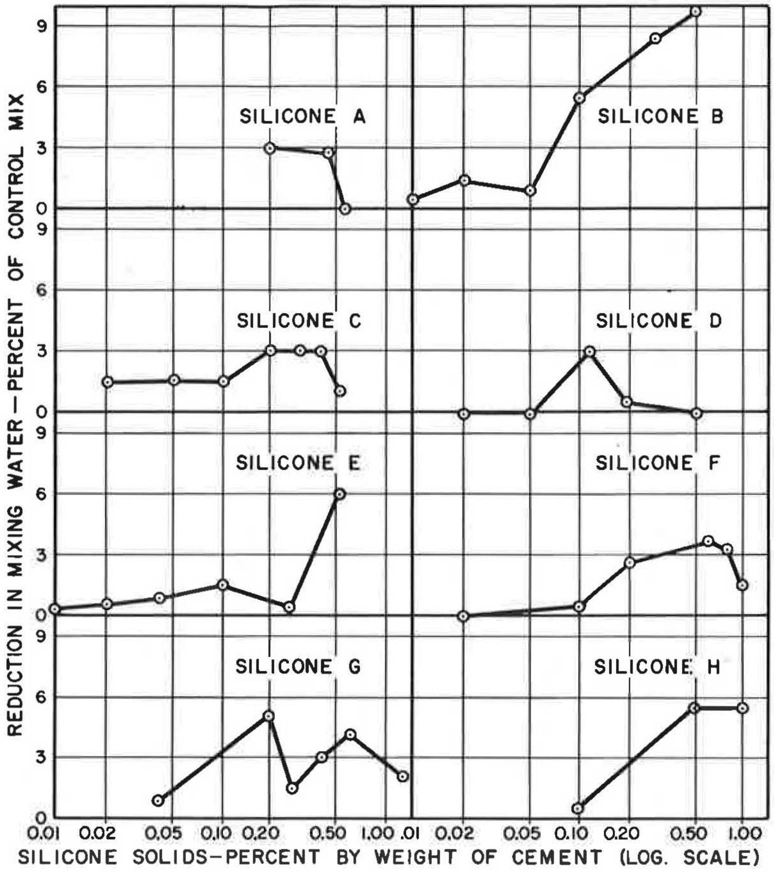

Figure 2. Effect of silicone on reduction in amount of mixing water, based on control mix.

RETARDATION OF SETTING TIME

The effect of various amounts of the silicone solutions on the retardation of the setting time of the concrete was determined by use of the Proctor penetration test (ASTM C 403). This test was made as described in a previous report on retarders (2). Retardation is the difference in time required for concrete prepared with the silicone admixtures and the control concrete made on the same day to support penetration loads of 500 psi. The results of these tests are given in Table 4. Readings were taken for about 15 hr or until about 11 PM. If the test specimens had not reached a penetration load of 500 psi by that time, the readings were resumed the next morning. Usually, the concrete had set up before then.

The results of these tests for a penetration load of 500 psi are shown in Figure 4. When silicones B, C, D, E, or F were used in amounts of only 0.05 percent silicone solids, the retardation was approximately 6 hr. When 0.2 percent silicone solids were used, the retardation was estimated to be about 12 hr. Further increase in the amount of silicone used is estimated to cause only a small increase in the retardation. It was estimated that, when 0.5 percent solids were used, the retardation would be between 15 and 20 hr. These five silicones are considered to retard the setting of the concrete more than would be desirable for normal construction purposes.

The use of 0.2 percent solids of silicones A and G retarded the setting of the concrete of 4 hr and ¾ hr, respectively, based on a 500-psi load in the Proctor test. Silicone H had no appreciable effect on the retardation of the concrete.

TABLE 3

MIX DATA[1]

Silicone			Slump (in.)	Reduction in Water[3] (%)	Air (%)	A.E.A.[4] (%)	Weight-Hardened Concrete[5] (pcf)
	Amount Used						
Iden.	Total Solids[2] (% by wt. of cement)	Liquid (oz./bag of cement)					
A	0.20	10	3.1	2.9	5.3	100	---
	0.40	20	3.3	2.9	5.7	100	---
	0.60	30	2.5	0	4.9	75	---
B	0.01	0.5	2.9	0.5	5.3	94	---
	0.02	1.0	3.1	1.4	5.5	94	---
	0.05	2.5	3.2	0.9	4.7	100	---
	0.10	5.0	3.0	5.4	4.9	80	---
	0.30	15.0	3.1	8.4	5.0	120	---
	0.50	25.0	3.3	9.9	5.5	160	---
C	0.02	1.0	3.2	1.6	5.0	93	---
	0.05	2.5	3.2	1.6	5.2	93	---
	0.10	5.0	3.2	1.5	5.0	80	---
	0.20	10.0	2.6	3.0	5.0	100	---
	0.30	15.0	2.9	3.0	5.0	117	---
	0.40	20.0	2.5	3.0	5.5	125	---
	0.50	25.0	3.0	1.1	5.1	174	---
D	0.02	1.0	2.5	0	5.0	100	---
	0.05	2.5	3.0	0	5.4	120	---
	0.10	5.0	2.7	3.0	5.5	117	---
	0.20	10.0	2.8	0.5	5.1	120	---
	0.50	25.0	2.8	0	5.4	140	---
E	0.01	0.5	2.9	0.4	5.9	65	148.7
	0.02	1.0	3.0	0.6	6.0	70	146.4
	0.04	2.0	3.0	0.9	6.8	80	144.2
	0.10	5.0	3.7	1.5	8.0	188	142.0
	0.25	12.5	4.2	0.4	4.7	200	139.5
	0.50	25.0	2.7	6.0	4.5	167	135.9
F	0.02	1.0	3.3	0	7.2	70	---
	0.10	5.0	3.2	0.5	6.8	70	---
	0.20	10.0	3.0	2.5	6.0	80	---
	0.60	30.0	3.5	3.8	4.2	287	---
	0.80	40.0	3.0	3.3	4.5	437	---
	1.00	50.0	3.5	1.5	4.5	313	---
G	0.040	1.5	3.2	0.9	6.3	50	---
	0.20	7.5	3.4	5.1	9±	0	---
	0.27	10.0	4.7	1.5	9±	80	---
	0.40	15.0	4.2	3.1	8.0	200	---
	0.60	20.0	2.9	4.2	5.1	100	---
	1.33	50.0	2.5	2.1	5.1	200	---
H	0.10	10	2.5	0.6	5.0	60	---
	0.50	50	3.0	5.4	8.5	187	---
	1.00	100	3.0	5.4	5.0	125	---

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[1] Control mix (avg. values): proportions = 94-200-300; cement = 6.0 bags per cu yd; slump = 3.0 in.; water = 5.58 gal per bag; air-entraining agent = 20.7 ml/bag; weight of hardened concrete = 149.1 pcf; and air content = 5.2%.

[2] Based on total solids for each silicone, from information furnished by producers, 30% solids for silicones A, B, C, D, E, and F, 40% for silicone G, and 15% for silicone H.

[3] Reduction in water as compared with that required for control mix made on same day.

[4] Relative amount of air-entraining agent used, amount used in control mix considered 100%.

[5] Weight determined on cylinders before testing for compressive strength.

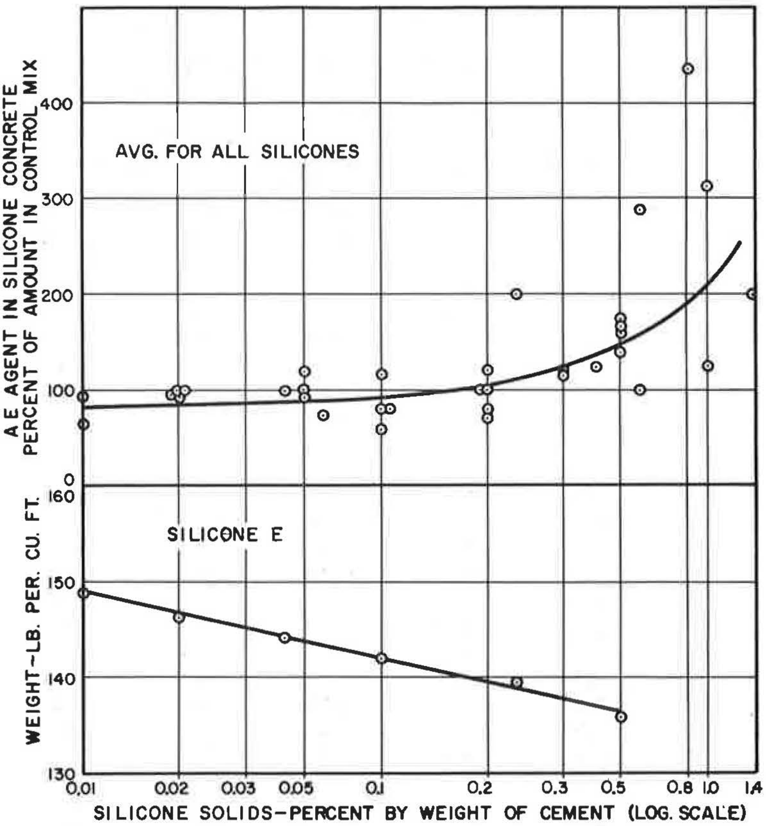

Figure 3. Effect of silicones on amount of AE agent needed and of one silicone on unit weight of concrete.

STRENGTH TESTS

Compressive strength tests were made at ages of 7 and 28 days on concrete prepared with various amounts of the silicone admixtures. These strengths were compared with the strengths of the control concrete made and tested on the same days. Table 4 gives the strength of the concrete prepared with silicone admixtures as the percentage of that of the corresponding control concrete. The relative compressive strengths at 28 days are shown in Figure 5.

Concrete prepared with all amounts of silicones A, B, C, and D (the sodium methylsiliconates) had higher strength than the control concrete in all cases except one.

When silicone E was used in amounts of less than 0.02 percent solids, the strengths were slightly higher than those obtained on the control mix. When amounts greater than 0.02 percent were used, the strengths decreased considerably as the amount of silicone used increased. When 0.50 percent solids were used, the strength was only 18 percent of the corresponding control mix. This loss in strength is related to the previously-mentioned foaming of the concrete.

For several mixes containing silicones F and G, the strengths were lower than for the control concrete. However, the data show that these mixes contained 6.0 percent or more air.

Only three amounts of silicone H were used. With 0.50 percent solids of this material, a reduction in strength of 21 percent was obtained. However, this mix had an air content of 8.5 percent. The other two mixes containing silicone H both showed slight reductions in strength.

TABLE 4

RESULTS OF RETARDATION AND STRENGTH TESTS

Silicone		Air (%)	Proctor Penetration Test, Retardation[1] at 500 Psi (hr:min)	Crushing Strength[2] (%)	
Iden.	Amount Total Solids Used (% by weight of cement)			7 Days	28 Days
A	0.20	5.3	4:15	107	114
	0.40	5.7	6:15	104	108
	0.60	4.9	6:30	100	111
B	0.01	5.3	1:30	104	104
	0.02	5.5	2:30	105	104
	0.05	4.7	6:45	112	106
	0.10	4.9	12[3]	116	119
	0.30	5.0	--	110	114
	0.50	5.5	--	107	111
C	0.02	5.0	2:35	107	105
	0.05	5.2	6:35	108	108
	0.10	5.0	11:30[3]	108	113
	0.20	5.0	--	113	112
	0.30	5.0	--	109	110
	0.40	5.5	--	109	109
	0.50	5.1	15[3]	106	104
D	0.02	5.0	1:10	100	103
	0.05	5.4	5:00	102	103
	0.10	5.5	9:45	112	110
	0.20	5.1	--	105	106
	0.50	5.4	--	100	99
E	0.01	5.9	2:20	106	104
	0.02	6.0	5:15	102	99
	0.04	6.8	8:40	100	91
	0.10	8.0	--	65	67
	0.25	4.7	--	21	18
	0.50	4.5	--	18	17
F	0.02	7.2	3:45	95	99
	0.10	6.8	10[3]	97	95
	0.20	6.0	11[3]	114	109
	0.60	4.2	12[3]	113	111
	0.80	4.5	--	102	99
	1.00	4.5	--	93	95
G	0.04	6.3	0:35	95	92
	0.20	9±[4]	0:40	77	79
	0.27	9±[4]	1:35	72	69
	0.40	8.0	1:40	102	101
	0.60	5.1	2:10	107	111
	1.33	5.1	3:15	98	99
H	0.10	5.0	0	100	96
	0.50	8.5	0:20	79	78
	1.00	5.0	0:05	90	90

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[1] Delay in time of hardening of concrete containing silicones as compared with control concrete made on same days; average time for control concrete to reach Proctor penetration load of 500 psi was 4 hr 15 min, and 7 hr 20 min for 4,000 psi.

[2] Ratio of strength of concrete containing silicones to strength of control concrete made on same day; average strength of control concrete was 4,140 psi at 7 days and 5,220 psi at 28 days.

[3] Estimated.

[4] Content high, strength values disregarded.

Except for silicones E and H, there appears to be an optimum amount of the other silicones which gives the maximum strength.

LABORATORY FREEZING AND THAWING TESTS

Laboratory freezing and thawing tests were made on a number of the mixes included in the strength tests. The tests were made on 3- by 4- by 16-in. beams frozen in air and thawed in water in accordance with ASTM Method C 291. These tests were continued through 1,000 cycles of freezing and thawing (at 300 cycles, only one of the mixes showed a loss in N^2 of over 10%). Table 5 gives the durability factors of the concretes prepared with the various silicones at 1,000 cycles as well as of the control mix. In addition, the relative durability factor is also given for

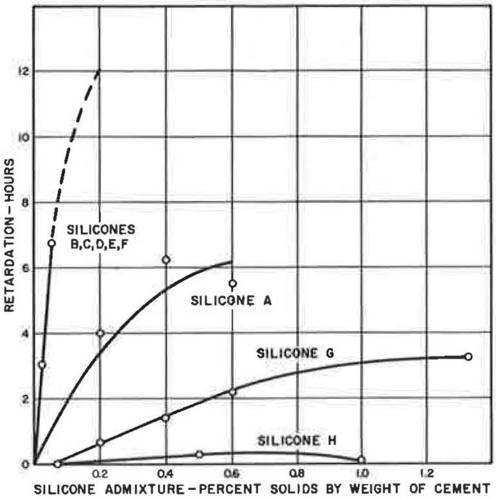

Figure 4. Relation between amount of silicone added and retardation.

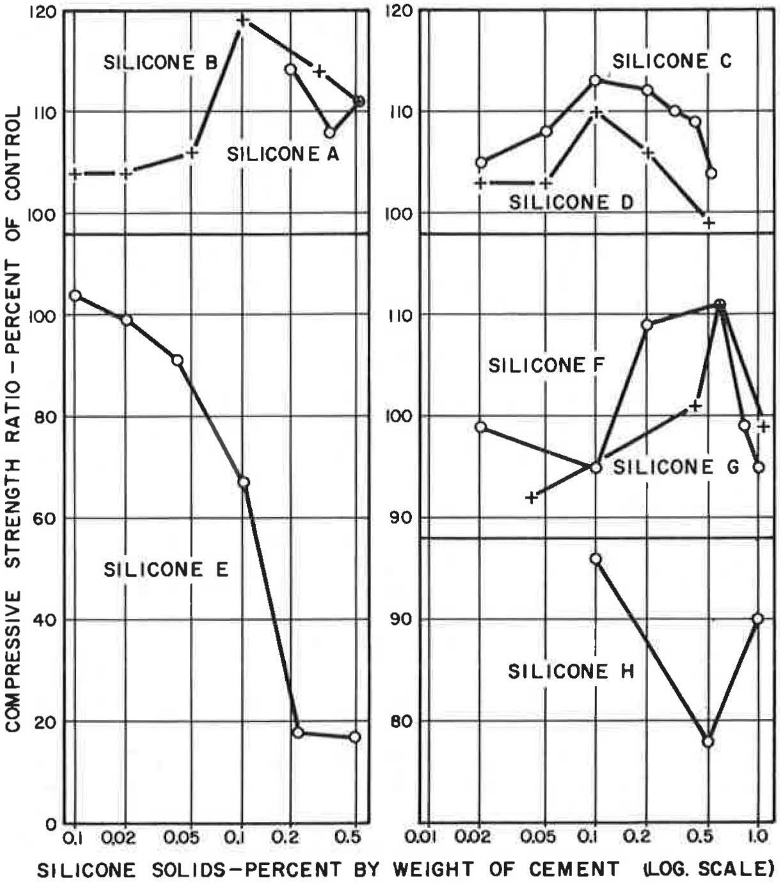

Figure 5. Effect of silicones on 28-day compressive strength.

TABLE 5

LABORATORY FREEZING AND THAWING[1]

Silicone		Air (%)	Durability Factor[2] (%)	Relative Durability Factor[3] (%)
Iden.	Amount Total Solids Used (% by weight of cement)			
Control	None	5.1	83	---
A	0.05	5.8	92	111
B	0.01	5.3	91	110
	0.02	5.5	90	108
	0.05	5.7	93	112
	0.10	4.9	83	100
	0.30	5.0	82	99
	0.50	5.5	81	98
C	0.02	5.0	82	99
	0.05	5.2	80	96
	0.20	6.5	87	105
	0.50	6.1	74	107
E	0.01	5.9	91	110
	0.04	6.4	89	107
F	0.02	7.2	94	113
	0.10	6.8	92	111
	0.20	6.0	75	90
G	0.20	9±	81	98

[1] Each value an average of tests on three 3- by 4- by 16-in. beams. Beams frozen and thawed in accordance with ASTM Method C 291.

[2] Based on loss in N^2 after 1,000 cycles of freezing and thawing.

[3] Ratio of durability factor of concrete containing silicone to durability factor of control concrete made on same day.

each mix. This is the ratio of the durability factor of the silicone concrete to that of the control mix. A relative durability of 80 percent or more for concrete prepared with admixtures is acceptable, as is specified in AASHO Specification M 154 for air-entraining admixtures and is in the proposed specification for retarders of Subcommittee III-h of ASTM Committee C-9 (ASTM Designation C 494-62 T). On this basis, all the silicones used are acceptable. There appears to be an optimum amount of silicone admixture for maximum durability. However, these tests are too limited to develop this quantity.

OUTDOOR SCALING TESTS

Outdoor exposure tests were made on 16- by 24- by 4-in. slabs to determine the effect of silicone admixtures on the resistance of concrete to scaling caused by de-icing agents. A description of the test is given elsewhere (1). The same report gives the results of tests in which silicone similar to silicone A was used. Those tests show that the use of silicone in proper amounts was effective in preventing scaling.

Similar tests were made using silicones B and C. At the time this report was prepared, these specimens had been exposed for only one winter. At the last inspection, neither the control nor the slabs containing silicone showed any appreciable amount of scaling. All were given a rating of less than 2. These tests are being continued.

SUMMARY

The four silicones classified as sodium methylsiliconates (silicones A, B, C, and D) gave the best results. These materials were all furnished in about the same concentration (about 30% solids). Three (B, C, and D) retarded the setting time of the concrete much more than would be desirable for ordinary usage.

From the available data, if these three silicones had been used in amounts of 0.2 percent silicone solids by weight of the cement, the retardation of set would have been over 10 hr. With this same amount, the retardation caused by silicone A was only 4 hr. Concretes having 10 to 20 percent higher strength than the control mixes were obtained with all four silicones. The most favorable results were obtained with 0.1 to 0.2 percent silicone solids. Freezing and thawing tests in the laboratory showed concretes prepared with silicones A, B, and C to have practically the same or greater durability than the control concrete. Tests for durability were not made on concretes prepared with silicone D due to lack of material.

The two silicones classified as alkyl silane esters (silicones E and F) were unstable. It was not possible to determine the amount of total solids in these solutions because of the volatility of the silicone materials. These two silicones used as an admixture caused excessive retardation of the setting time of the concrete. Silicone E caused a reduction in the concrete strength due to foaming during hardening. There was a corresponding reduction in the weight of the hardened concrete. Concrete prepared with silicone F had strengths 10 to 15 percent greater than that of the control concrete when 0.2 to 0.6

percent solids were used. There is no apparent reason for the differences in the behavior of these two similar materials. Concrete prepared with either of these materials had good durability, but only a few mixes were tested and these all contained more air than the control concrete.

The use of silicones G and H, which were classified as silicone resin emulsions, had beneficial effects on the properties of the concrete only in isolated cases. They gave unpredictable results on reduction in mixing water and air content. It appears that if either were used in construction, very careful control of the amount of silicone would be required. Silicone G caused only a modest amount of retardation of setting time of concrete, whereas silicone H had practically no effect. When used in amounts which did not give excessive amounts of entrained air, both silicones furnished concretes having 90 to 109 percent of the strength of the control concrete. Only one concrete prepared with silicone G was tested for resistance to freezing and thawing. Although this concrete had low strength, its air content was high and the relative durability was almost equal to that for the control concrete.

The retardation of the setting time offers a problem that must be resolved before this material can be used commercially. However, the tests reported here show that, when some of these silicones are used as admixtures in concrete, both the strength and durability of the concrete will be improved.

CONCLUSIONS

Based on tests using only one brand of cement, the results of the tests warrant the following conclusions. These conclusions apply specifically to concrete prepared with the materials, mixes, and mixing procedures described in this paper.

1. When used as admixtures in certain amounts, solutions of sodium methylsiliconates increased the compressive strength and durability of concrete.
2. The alkyl silane esters and the silicone resin emulsion types of silicones in most cases either had no effect or were detrimental to the compressive strength and durability of concrete.
3. There appears to be a critical amount of silicone admixture needed to obtain maximum compressive strength or durability of the concrete. This amount varies with the properties of the silicones.
4. In most cases, silicones retarded the setting time of the concrete. In the majority of cases, when the silicones were used in amounts needed to obtain maximum strength or durability of concrete, the retardation of the set was greater than can be tolerated for normal construction purposes.
5. The use of silicones as admixtures had no appreciable effect on the water required for a given slump or on the air content of the concrete.

REFERENCES

1. Grieb, W. E., Werner, G., and Woolf, D. O., "Resistance of Concrete Surfaces to Scaling by De-Icing Agents." Public Roads, 32:3 (Aug. 1962).
2. Grieb, W. E., Werner, G., and Woolf, D. O., "Water-Reducing Retarders for Concrete." Public Roads, 3:6 (Feb. 1961).

Discussion

HOWARD NEWLON, JR., Highway Research Engineer, Virginia Council of Highway Investigation and Research.—The data presented in the paper certainly show that there can be considerable variation in the effects of the various materials marketed as silicones and that at the present state of development there is very little to justify their acceptance for use in highway concrete. It would appear that whatever benefit is derived from the admixture is largely the result of its ability to effect water reduction.

In this regard it is of interest to compare some of the data presented by Mr. Grieb with some limited data developed by the writer using a silicone commercially available under the same trade name as that designated silicone B in the paper.

TABLE 6

CEMENT ANALYSIS

Computed Compound Composition				Other Oxides				Fineness (Blaine)
C_3A	C_3S	C_2S	C_4AF	SO_3	Na_2O	K_2O	$Na_2O_{(eq.)}$	
5	42	34	13	1.80	0.09	0.55	0.45	3,450

This silicone was used as an admixture in concrete which in mix proportions and characteristics was essentially like that studied by Mr. Grieb. The only important differences were that the cement was Type II with the characteristics shown in Table 6 and the coarse aggregate was a natural siliceous gravel. The silicone was added with the mixing water to give a concentration of 0.3 percent by weight of cement, the dosage recommended by the manufacturer.

In these tests it was found that a significant water reduction was obtained for the admixtured concrete as compared with plain concrete having the same slump. The average water reduction based on 4 replicate batches for each condition was 13 percent. The data in Figure 2 would indicate a water reduction of almost 9 percent for the same silicone dosage. In spite of usual between-laboratory variation, the differences in the data are not great, considering the differences between aggregates and cements. For example, admixtures such as these are usually more effective with Type II than with Type I cements. The strength data reflected the effects of this water reduction. The extended delay of setting found by Grieb was also found in our tests.

It appears from both sets of data that silicone B causes a water reduction that increases with silicone content, whereas the other sodium methylsiliconate types do not. Table 1 and Figure 1 indicate that silicones A, B, and C are essentially the same. The difference in performance of silicone B would indicate that there is some characteristic that has not been detected. It might be that pursuit of this matter by those interested would lead to an improvement of performance as well as a better understanding of the mechanism of action of these materials.

Freeze-Thaw and Scaling Tests on Silicone-Treated Concrete

D. J. T. HUSSELL, Concrete Testing Engineer, Materials and Research Division, Department of Highways, Ontario

Laboratory tests of freeze-thaw durability and scaling resistance of concretes treated with silicone water repellents indicated that the silicone gave no appreciable benefit to air-entrained concrete; a slight improvement was noted in the durability and scaling resistance of silicone-treated non-air-entrained concrete.

• IN 1957, the Ontario Department of Highways started using a sprayed silicone water repellent as a protective coating on new structures, both on exposed surfaces and on deck sections which were subsequently covered with asphalt. The use of silicones was introduced after the reported success with these materials on the New York Thruway (1) where it was found that the silicone-treated concrete had greater resistance to salt scaling and improved light reflectance.

When used as a protective coating, silicone is in the form of a resin derived from alkylchlorosilanes and dissolved in a hydrocarbon solvent, or, alternatively, a water-soluble sodium siliconate may be used. In either case, the liquid is brushed or sprayed onto the surface, the silicone reacts with the surface, and the solvent evaporates leaving a water-repellent surface.

This reaction produces a surface that is water repellent but not sealed against water penetration. Because there were very few data available to indicate what degree of protection from freeze-thaw and scaling action might be expected, the Materials and Research Division undertook a series of laboratory tests to compare the freeze-thaw and scaling resistance of silicone-treated and untreated concrete. Several different testing and curing procedures were used in an attempt to simulate different field conditions, but the effectiveness of silicone in preventing moisture penetration beneath asphalts was not investigated.

The tests described in this paper were started in 1958 and completed early in 1960.

SILICONES TESTED

No attempt was made to evaluate individual commercial silicone products. Two materials were used in the tests: (a) the silicone resin type in a hydrocarbon solvent and (b) a water-soluble sodium siliconate. The silicone resin in hydrocarbon solvent (silicone 1) according to the manufacturer's data sheet contains 5 to 8 percent undiluted silicone resin. The water-soluble sodium siliconate (silicone 2), supplied concentrated, contains according to the manufacturer's data sheet 30 percent total solids and 20.5 percent silicone.

The percentage of solids in the samples was 4.8 percent for silicone 1 and 32.8 percent for silicone 2.

Silicone 1 was applied as supplied by the manufacturer. Silicone 2 was diluted 1 part to 12.4 parts of water by volume, giving a 2.8 percent solids solution assuming 30 percent solids in the concentrate, or 3.1 percent solids taking 32.8 percent solids in the concentrate.

The materials were applied by brush according to the manufacturer's instructions, sufficient material being brushed onto the surface of each specimen to give a coverage

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Paper sponsored by Committee on Effect of Ice Control.

TABLE 1

CONCRETE STONE AND SAND SPECIFICATIONS

Stone		Sand	
Sieve Size	Cumulative % Passing	Sieve Size	Cumulative % Passing
1-in.	100	No. 4	100
¾-in.	90-100	No. 8	80-100
⅝-in.	65-90	No. 14	50-85
⅜-in.	20-55	No. 28	25-60
No. 4	0-10	No. 48	5-30
		No. 100	0-10
		No. 200	0-3

TABLE 2

CURING PROCEDURES

Curing Procedure	Moist Curing (days)	Dry Curing (days)	Time of Silicone Application (days)
1	28	-	28
2	21	14	35
3	35	-	28
4	21	21	35

of approximately 180 sq ft per imperial gallon. In all cases, this was more solution than could be readily absorbed by the surface, although dry surfaces absorbed the solution more readily than wet ones.

FREEZE-THAW TESTS

Materials Tested

Normal portland cement was used. Two combinations of aggregate from Ontario were used: (a) crushed gravel (Brighton) and natural sand (Caledon), and (b) crushed rock (Hagersville) and natural sand (Paris). The air-entraining agent was neutralized Vinsol resin. Results of routine tests on these materials are given in the Appendix. Both silicone 1 and 2 were used.

Fabrication of Specimens

The aggregates were graded to meet the Department's specifications for ¾-in. concrete stone and concrete sand (Table 1). All mixes were proportioned to produce concrete containing approximately 6 bags of cement per cu yd of concrete (based on Canadian bag of cement = 87.5 lb). The sand contents were varied slightly according to the air content anticipated and the water contents were adjusted to give 3 ± ½-in. slump in all cases.

Nine 3- by 4- by 16-in. beams were made from each mix: three to receive no silicone treatment (treatment A), three to be coated with silicone 1 (treatment B), and three to be coated with silicone 2 (treatment C). Each group of three beams was compacted by vibrating for 15 sec with an external vibrator. The beams were removed from the molds 24 hr after placing.

Curing

Four different curing procedures were used (Table 2) involving different periods of moist curing at 72 F and 100 percent relative humidity, and air drying in the laboratory. Testing commenced immediately on completion of the curing period indicated.

Testing Procedure

Two test procedures were used: (a) freezing and thawing in water, and (b) freezing in air and thawing in water. The beams were subjected to freezing and thawing in an automatic freeze-thaw machine, giving 8 cycles of freezing and thawing per day between 0 F and 40 F. The procedures used were substantially in agreement with ASTM methods C290-57T, "Tentative Method of Test for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water," and C291-57T, "Tentative Method of Test for Resistance of Concrete Specimen to Rapid Freezing in Air and Thawing in Water."

From time to time (usually about every 24 cycles) the beams were removed from the freeze-thaw machine during a thawing cycle and were tested for change in weight, length, and relative dynamic modulus of elasticity. Testing continued for 300 cycles or until the beams disintegrated.

TABLE 3

FREEZE-THAW MIXES AND DURABILITY FACTORS

MIX NO.	DATE MADE	BATCH PROPORTIONS					TEST RESULTS				CURING PROCEDURE	TESTING PROCEDURE	SILICONE APPLIED	SILICONE TREATMENT	DURABILITY FACTOR
		CEMENT	C.A.	F.A.	WATER	A.E.A.	SLUMP	AIR CONTENT	CEMENT FACTOR	W/C RATIO					
—	d.m.y.	lb.	lb.	lb.	lb.	c.c.	inch	%	bags/ cu.yd.	—	—	—	days	—	—
10	3.3.58	29.1	105.4	76.4	15.0	—	$3\frac{1}{2}$	—	N.T.	0.49	1	1	—	A	N.T.
													28	B	N.T.
													28	C	N.T
11	6.3.58	29.1	105.4	76.4	15.0	—	3	—	N.T	0.49	2	1	—	A	N.T
													35	B	N.T
													35	C	N.T
12	6.3.58	29.1	105.4	71.5	13.6	5.5	$2\frac{7}{8}$	5.0	6.03	0.44	1	1	—	A	N.T
													28	B	N.T
													28	C	N.T
13	10.3.58	29.1	105.4	71.5	13.6	5.5	$2\frac{1}{2}$	5.0	6.12	0.44	2	1	—	A	N.T
													35	B	N.T
													35	C	N.T
14	19.12.58	29.1	105.4	76.4	15.7	—	$3\frac{1}{4}$	—	6.00	0.51	1	2	—	A	V.L
													28	B	V.L
													28	C	V.L
15	2.12.58	29.1	105.4	76.4	15.0	—	$2\frac{7}{8}$	—	5.95	0.49	2	2	—	A	~ 10
													35	B	~ 12
													35	C	~ 20
16	19.12.58	29.1	105.4	71.5	15.7	5.5	3	5.0	5.96	0.51	1	2	—	A	96.9
													28	B	97.5
													28	C	98.8
17	2.12.58	29.1	105.4	71.5	14.8	5.5	3	5.0	6.00	0.48	2	2	—	A	96.3
													35	B	97.4
													35	C	98.6
30	4.3.59	29.1	105.4	74.0	14.9	2.5	3	4.0	6.00	0.49	3	2	—	A	98.6
													28	B	98.7
													28	C	99.8
31	4.3.59	29.1	105.4	74.0	14.9	2.5	3	3.9	6.00	0.49	4	2	—	A	102.5
													35	B	102.5
													35	C	102.7
32	18.8.59	29.1	105.4	76.4	15.0	—	$2\frac{5}{8}$	—	5.95	0.49	3	2	—	A	~20
													28	B	~40
													28	C	~30
33	18.8.59	29.1	105.4	76.4	15.1	—	$2\frac{3}{4}$	—	5.87	0.49	4	2	—	A	64.4
													35	B	~ 37
													35	C	~35
34	20.8.59	29.1	105.4	71.5	14.6	5.8	$3\frac{1}{2}$	6.2	5.90	0.48	3	2	—	A	100.3
													28	B	99.9
													28	C	99.2
35	25.8.59	29.1	105.4	71.5	14.7	5.8	$3\frac{1}{4}$	6.0	5.90	0.48	4	2	—	A	101.7
													35	B	100.8
													35	C	101.6
36	25.8.59	29.1	105.4	76.4	15.6	—	$2\frac{3}{4}$	—	5.90	0.51	3	1	—	A	~ 5
													28	B	~15
													28	C	~ 5
37	28.8.59	29.1	105.4	76.4	15.7	—	$3\frac{1}{2}$	—	5.90	0.51	4	1	—	A	~16
													35	B	~15
													35	C	~20
38	2.10.59	29.1	105.4	74.0	16.1	2.2	$3\frac{1}{8}$	3.0	6.00	0.53	3	1	—	A	85.4
													28	B	87.0
													28	C	80.8
39	2.10.59	29.1	105.4	74.0	16.0	2.2	$3\frac{1}{4}$	3.2	6.00	0.53	4	1	—	A	77.5
													35	B	86.7
													35	C	84.6
40	2.10.59	29.1	105.4	71.5	15.0	6.3	3	4.5	6.00	0.49	3	1	—	A	96.9
													28	B	93.2
													28	C	96.2
41	2.10.59	29.1	105.4	71.5	15.1	5.8	3	4.5	6.00	0.49	4	1	—	A	76.5
													35	B	77.3
													35	C	79.0
42	23.10.59	29.1	93.5	79.1	16.4	5.4	$2\frac{7}{8}$	4.2	6.00	0.54	4	2	—	A	64.4
													35	B	77.3
													35	C	77.5
43	23.10.59	29.1	93.5	79.1	15.9	5.4	3	4.2	6.05	0.52	3	2	—	A	22
													28	B	25
													28	C	30.5

NOTES:

1. Aggregates.
Mixes Nos. 10-17 & 30-41
C.A. Brighton.
F.A. Caledon.
Mixes Nos. 42 & 43
C.A. Hagersville
F.A. Paris.

2. W/C ratio approximate. Absorption of aggregates assumed to be 0.4 %

3. Curing Procedures
(1) 28 days moist
(2) 21 days moist + 14 days dry.
(3) 35 days moist.
(4) 21 days moist + 21 days dry.

4. Testing Procedures.
(1) Freeze and Thaw in Water.
(2) Freeze in Air and Thaw in Water.

5. Silicone Treatment.
(A) None
(B) Silicone 1
(C) Silicone 2

6. Durability Factor.

$$D.F. = \frac{PN}{M}$$

where P = relative dynamic modulus of elasticity at N cycles, percent.
N = number of cycles at which P = 60 or 300, whichever occurs first.
M = 300 cycles.

7. N.T. = Not Tested.
V.L. = Very low.

Tests and Results

Details of all freeze-thaw tests are shown in Table 3. In the first group of mixes (Nos. 10-17), curing procedures 1 and 2 were used in combination with the two testing procedures for air-entrained and non-air-entrained concretes. The second group of mixes (Nos. 30-41) was similar to the first group except that curing procedures 3 and

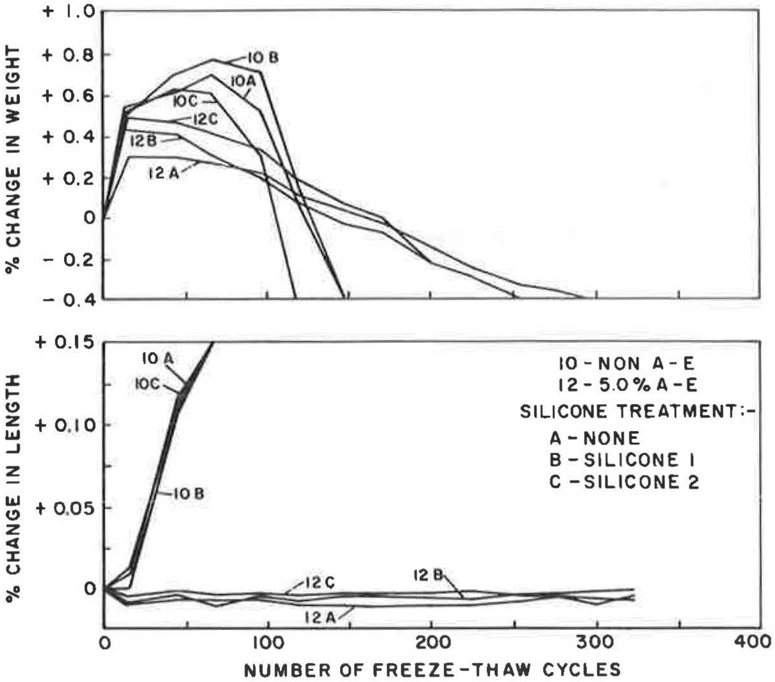


Figure 1. Effect of silicone treatment on freeze-thaw durability of air-entrained and non-air-entrained concrete, 28 days moist, freeze and thaw in water.

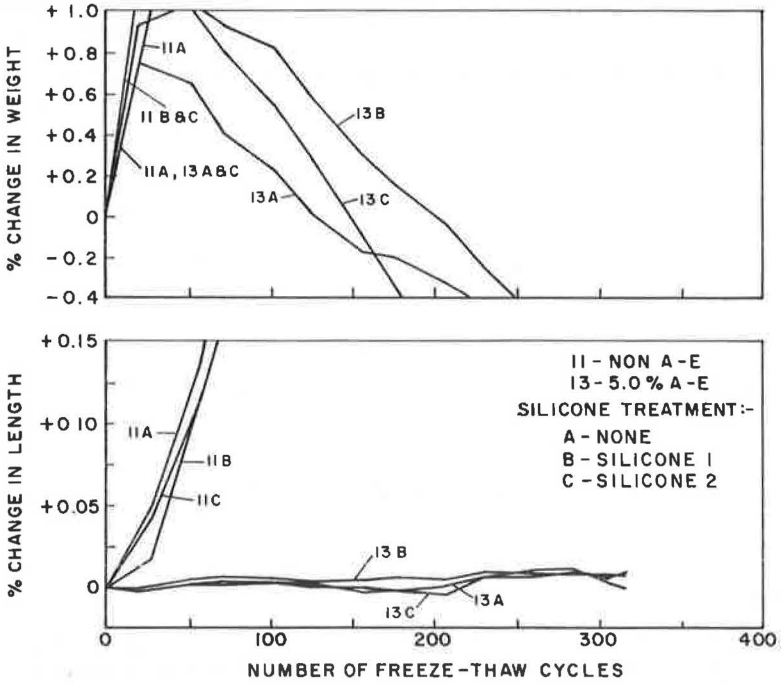


Figure 2. Effect of silicone treatment on freeze-thaw durability of air-entrained and non-air-entrained concrete, 21 days moist + 14 days dry, freeze and thaw in water.

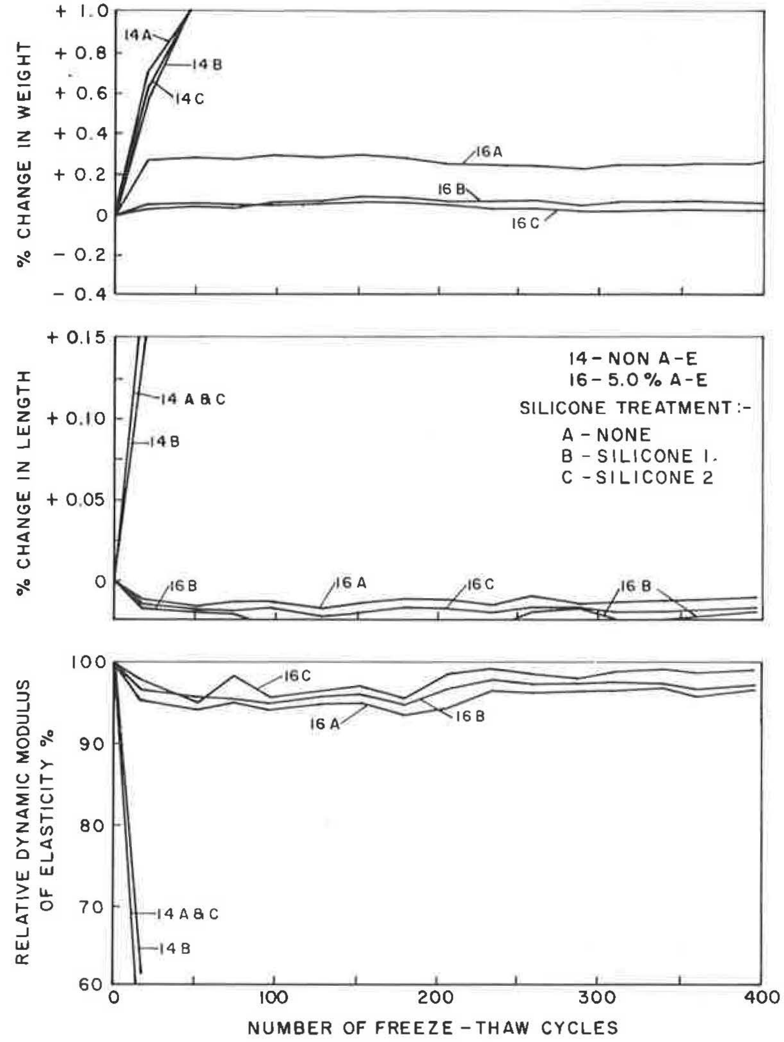


Figure 3. Effect of silicone treatment on freeze-thaw durability of air-entrained and non-air-entrained concrete, 28 days moist, freeze in air and thaw in water.

4 were used, thus allowing a longer period for the silicone to cure; an additional set of mixes with less entrained air was included in this series (Nos. 30, 31, 38, and 39). Mixes 42 and 43 were made with a coarse aggregate which contained a high proportion of chert, to determine whether silicone treatment would improve the freeze-thaw resistance of this material.

The results of tests for change in weight, length, and relative dynamic modulus of elasticity are shown in Figures 1 through 12 and average durability factors are given in Table 3.

SCALING TESTS

Materials Tested

Normal portland cement was used. The aggregate consisted of crushed gravel from Brighton, Ont., and natural sand from Paris, Ont. The admixture was neutralized Vinsol resin. Results of routine tests on these materials are given in the Appendix. Also, silicones 1 and 2 were both used.

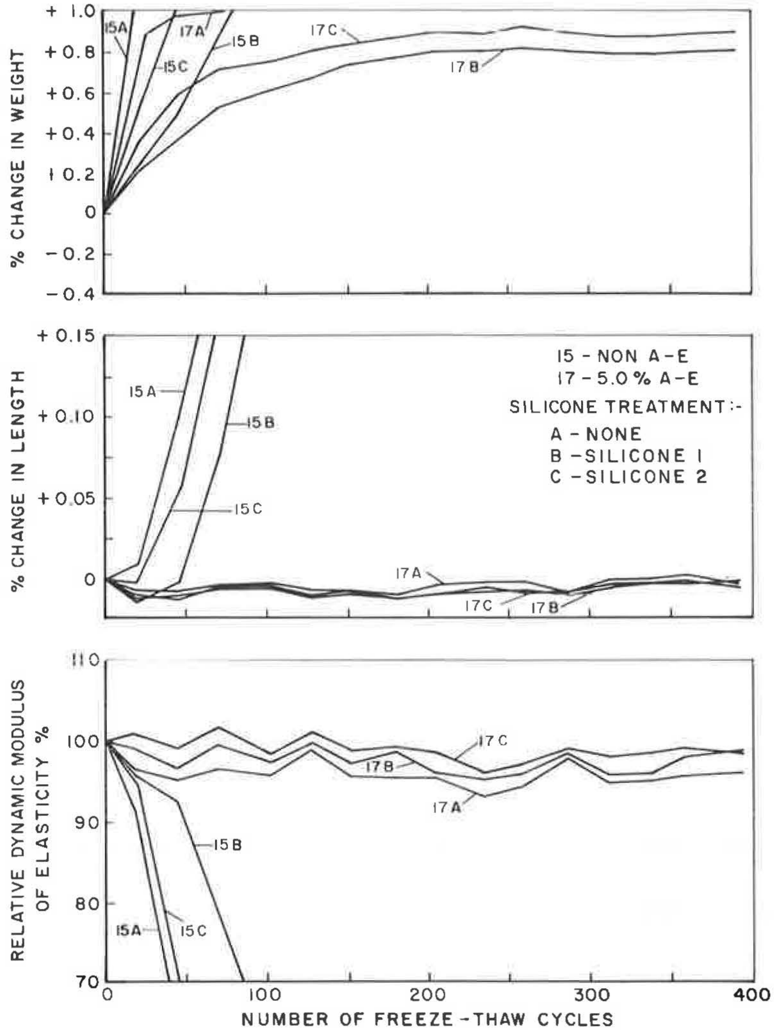


Figure 4. Effect of silicone treatment on freeze-thaw durability of air-entrained and non-air-entrained concrete, 21 days moist + 14 days dry, freeze in air and thaw in water.

TABLE 4

STONE AND SAND PROPORTIONS

Stone		Sand	
Sieve Size	Cumulative % Passing	Sieve Size	Cumulative % Passing
1-in.	100	No. 4	100
3/4-in.	90	No. 14	65
1/2-in.	60	No. 28	40
3/8-in.	30	No. 48	15
No. 4	0	No. 100	5

Fabrication of Specimens

To give close control over grading, the stone was divided into four sizes and the sand into five, and recombined in the porportions given in Table 4.

All mixes were proportioned to produce concrete containing approximately 6 bags of cement per cu yd of concrete (based on Canadian bag of cement = 87.5 lb). The sand contents were varied slightly according to the air content anticipated, and the water contents were adjusted to give 3 ± 1/2-in. slump in all cases.

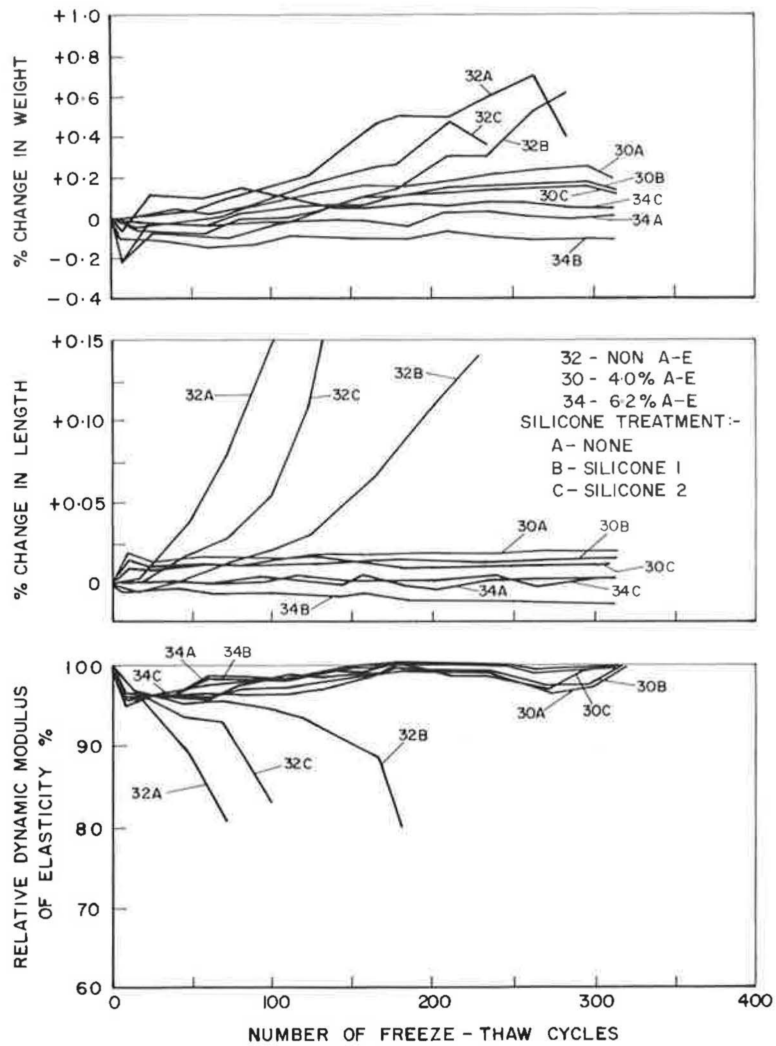


Figure 5. Effect of silicone treatment on freeze-thaw durability of air-entrained and non-air-entrained concrete, 35 days moist, freeze in air and thaw in water.

Six slabs, each approximately 15 by 6 by 3 in., were made from each mix. The slabs were compacted by vibrating for 5 sec with an external vibrator. The surface was then struck off level with three passes of a wood float. After 2 hr, the surface of the slab was given a rough texture by making three passes with a stiff bristle brush. If any moisture was brought to the surface, the brushing was repeated at 3 hr.

After 24 hr of curing, the slabs were removed from the moist room and a mortar dike about ¾-in. high was cast around the edge of each slab. It was found that an air-entrained mortar made with pass 14 sand, bonded to the slab with an epoxy resin bonding agent, gave the most satisfactory results. After the dikes had been cast, the slabs were returned to the curing room.

Curing

All slabs were cured at 72 F and 100 percent relative humidity for 14 days, followed by 14 days dry curing in the laboratory at 72 F. Where required, the silicone coat

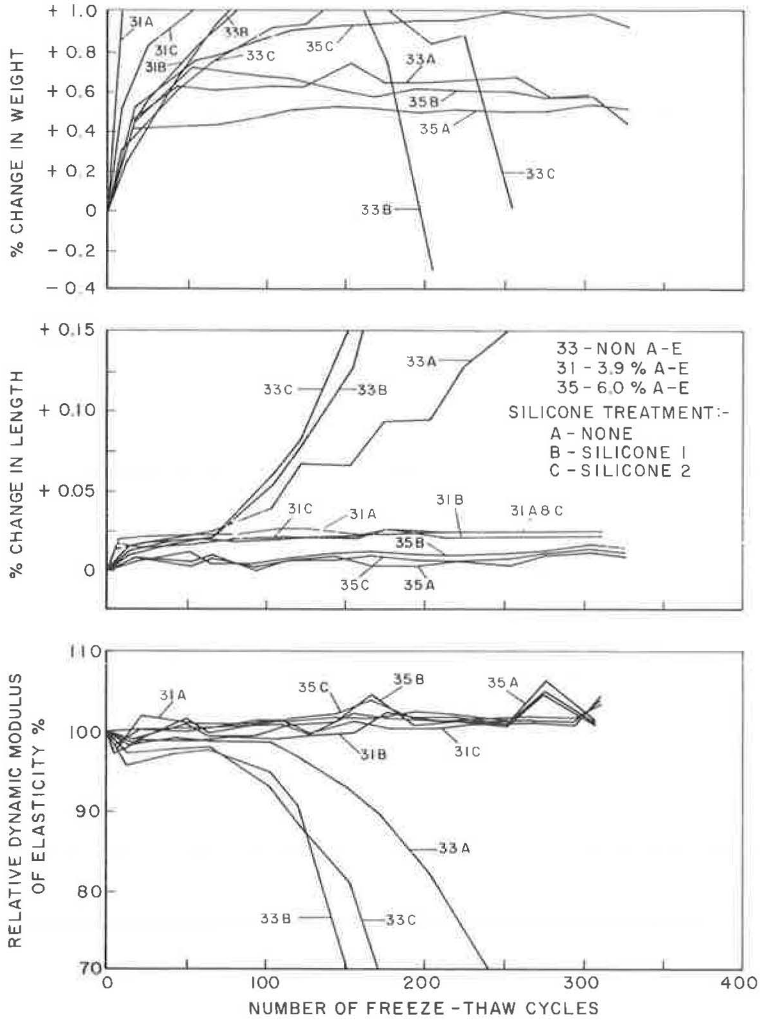


Figure 6. Effect of silicone treatment on freeze-thaw durability of air-entrained and non-air-entrained concrete, 21 days moist + 21 days dry, freeze in air and thaw in water.

was applied at 28 days, after which two different procedures were followed: (a) slabs were stored dry in the laboratory for 4 days, followed by 3 days covered to a depth of ¼ in. with water, and (b) slabs were stored dry in the laboratory for 7 days.

Testing Procedure

The test procedures used were based on those developed by Verbeck and Klieger (2). Two curing procedures were used and two testing methods, resulting in four different types of procedures.

In a similar testing procedure, Verbeck and Klieger found that the most severe conditions were obtained using 2 to 3 percent sodium chloride solution (by weight). Therefore, in this study a 3 percent sodium chloride solution was selected for use in all cases to give a severe test, and no attempt was made to study the effect of different solution strengths or of other de-icing agents.

Testing of all slabs began at an age of 35 days. Two test procedures were used:

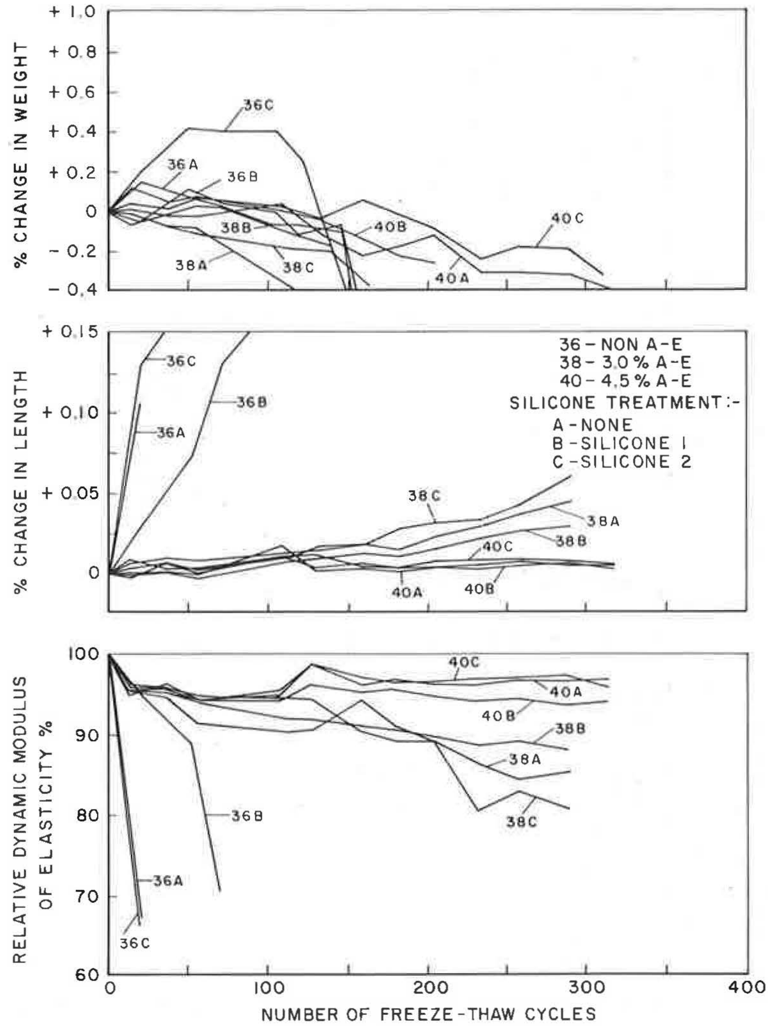


Figure 7. Effect of silicone treatment on freeze-thaw durability of air-entrained and non-air-entrained concrete, 35 days moist, freeze and thaw in water.

1. Freezing with de-ice solution on slab. At an age of 35 days the slabs were placed in a cold room at -10 F with a 3 percent sodium chloride solution covering the surface to a depth of $\frac{1}{4}$ in. At 9 AM on the following morning, the slabs were brought into the laboratory at 72 F and allowed to thaw until 4 PM at which time they were again placed in the cold room with the de-ice solution still on the surface. The procedure was repeated each day, the slab being rinsed and the de-ice solution replaced with fresh solution twice a week. The slabs were left in the freeze portion of the cycle over the weekends.

2. This method was the same as the preceding except that the thaw solution was placed on the slab after each freezing cycle and removed before the next freezing cycle. Thus the slab was frozen with the surface only slightly damp.

The slabs were examined periodically and given a rating from 0 to 5 according to the degree of surface scaling, by comparison with standard rated slabs prepared for the purpose. These ratings would probably approximate Verbeck and Klieger's (2) ratings: 0 = no scaling, 1 = very slight scaling, 2 = slight to moderate scaling, 3 =

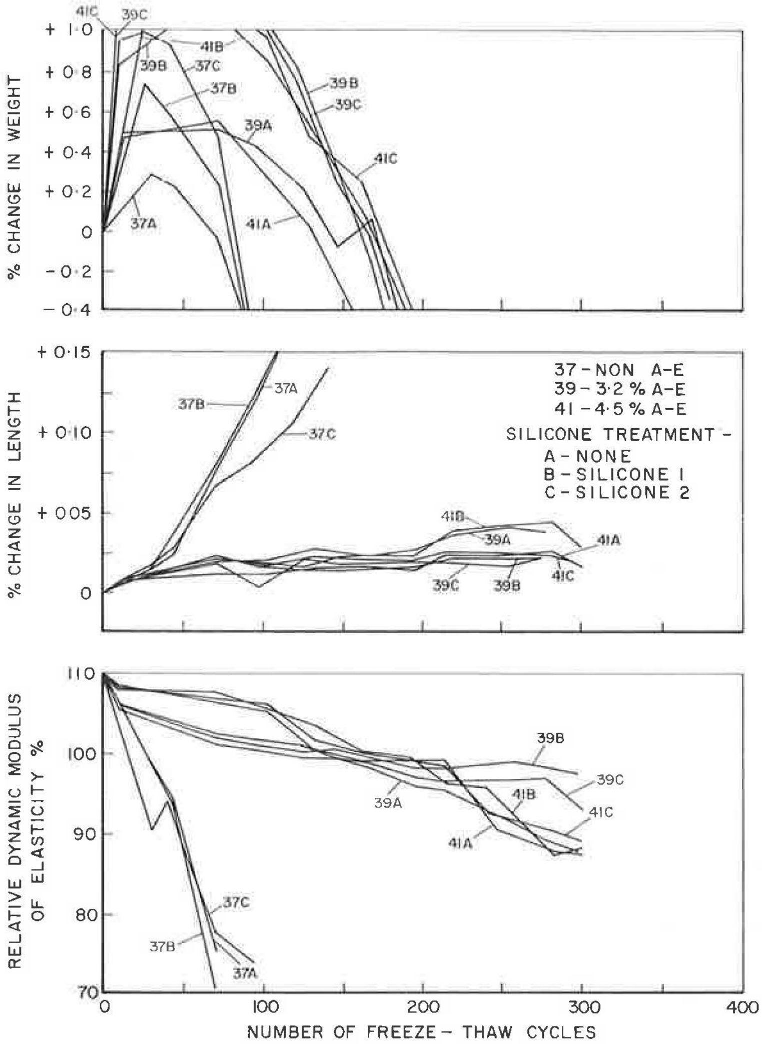


Figure 8. Effect of silicone treatment on freeze-thaw durability of air-entrained and non-air-entrained concrete, 21 days moist + 21 days dry, freeze and thaw in water.

moderate scaling, 4 = moderate to severe scaling, and 5 = severe scaling. The standard slabs are shown in Figure 13.

On some occasions, unsatisfactory dikes made it necessary to remove slabs from testing for a short period to make repairs. Two slabs were prepared for each condition of test and the average rating was plotted against the number of cycles of the scaling test.

Tests and Results

Details of the scaling tests are given in Table 5. For the first group of mixes (Nos. 22 to 25), curing procedure 1 was used, mixes 22 and 23 being non-air-entrained concrete and mixes 24 and 25 being air-entrained. Mixes 26 to 29 were repetitions of mixes 22 to 25, except for the different curing procedure. Mixes 46 and 47 were air-entrained but had a lower air content than the other air-entrained mixes, and were treated similarly to mixes 26 to 29.

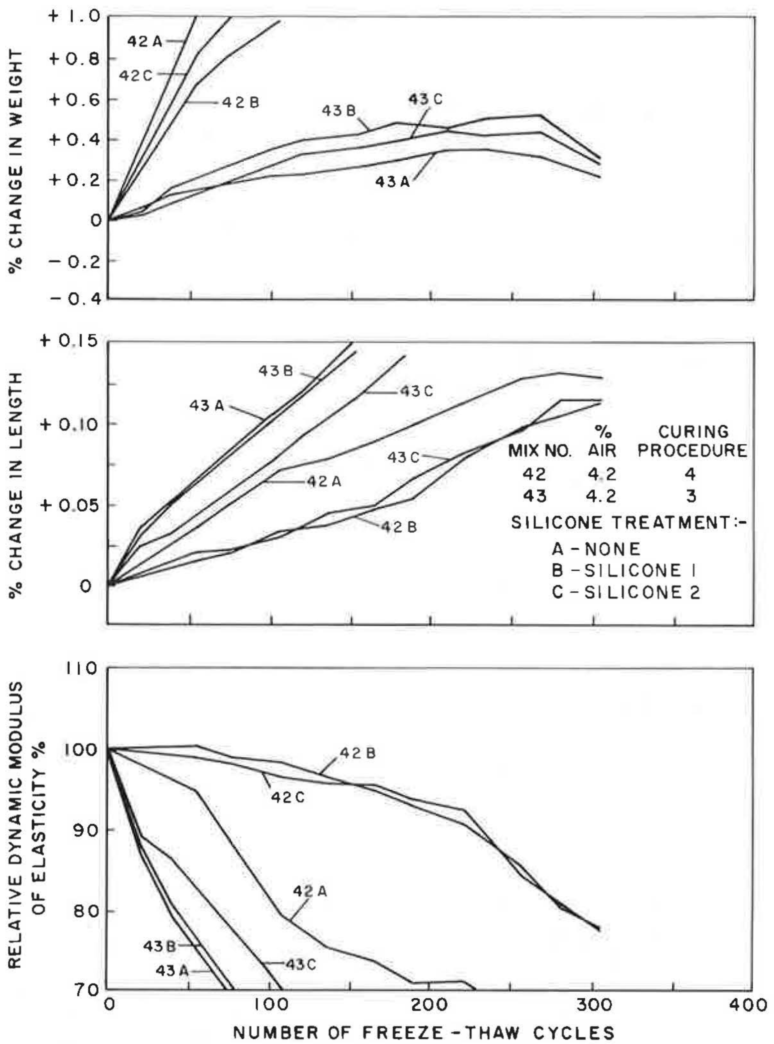


Figure 9. Effect of silicone treatment on freeze-thaw durability of air-entrained concrete using coarse aggregate of poor durability, freeze in air and thaw in water.

Results of the tests are given in Table 5 and plots of them are shown in Figures 14 and 15.

ANALYSIS

Freeze-Thaw Tests

The results of the freeze-thaw tests are given in Table 3 and Figures 1 to 12. In considering the effect of the silicone solution on freeze-thaw durability, it is advantageous to consider first the effect of the different curing and testing procedures on the durability of untreated non-air-entrained and air-entrained concrete. Results of tests on untreated concrete are compared in Figures 10 to 12.

Figure 10 shows the effect of different curing procedures for concrete tested by freezing in air and thawing in water. The non-air-entrained concrete subjected to a period of dry curing (mix 33A) shows much greater durability than similar concrete that was continuously moist cured before testing (mix 32A). Air-entrained concretes

TABLE 5

SCALING MIXES AND RESULTS OF SCALING TESTS

MIX NO.	DATE MADE (1959)	BATCH PROPORTIONS					TEST RESULTS				CURING PROCEDURE	TEST PROCEDURE	SILICONE TREATMENT	NUMERICAL SCALE RATING AT INDICATED NUMBER OF CYCLES (Bracketed figures are Nº of cycles at which a rating 5 was reached.)						
		CEMENT	STONE	SAND	WATER	A. E. A.	SLUMP	AIR CONTENT	CEMENT FACTOR	W/C RATIO				5	15	25	50	75	100	150
	d m	lb.	lb.	lb.	lb.	c. c.	inch.	%	bags/ cu.yd.	—	—	—	—	—	—	—	—	—	—	—
22	24.2	27.2	97.3	71.1	14.0	-	$2\frac{5}{8}$	—	6.01	0.49	1	1	A	1.5	2.75	3.75	(30)	-	-	-
													B	0	1.5	2.25	3.25	3.75	4.0	4.75
													C	1.25	1.75	2.75	3.25	3.75	4.25	(124)
23	24.2	27.2	97.3	71.1	14.0	-	$2\frac{5}{8}$	-	6.01	0.49	1	2	A	1.0	1.5	1.5	1.5	1.5	1.5	1.75
													B	0	0	0.25	0.5	0.5	0.5	1.0
													C	0	0	0.25	0.5	0.75	0.75	1.25
24	24.2	27.2	97.3	66.8	13.0	5.0	3	5.2	6.07	0.45	1	1	A	1.0	1.5	1.5	1.5	1.75	2.5	2.5
													B	0	0.75	1.25	1.75	2.75	2.75	2.75
													C	0.5	1.25	1.25	1.25	2.0	2.25	2.5
25	24.2	27.2	97.3	66.8	13.0	5.0	3	5.7	6.04	0.45	1	2	A	0	0	0	0	0.5	0.5	0.5
													B	0	0	0	0	0.5	0.5	0.5
													C	0	0	0.25	0.25	0.5	0.5	0.5
26	9.3	27.2	97.3	71.1	14.3	-	$3\frac{1}{8}$	-	5.99	0.50	2	1	A	1.5	2.75	3.75	4.5	(63)	-	-
													B	0.5	1.5	1.75	2.5	3.0	3.5	4.75
													C	1.0	1.75	2.0	3.5	3.75	4.25	(126)
27	9.3	27.2	97.3	71.1	14.5	-	$3\frac{1}{2}$	-	6.00	0.51	2	2	A	0	0	0	0.5	0.5	0.5	0.75
													B	0	0	0	0.5	0.5	0.5	0.75
													C	0	0	0.25	0.25	0.5	0.5	0.5
28	9.3	27.2	97.3	66.8	13.5	5.0	$3\frac{1}{8}$	5.9	6.00	0.47	2	1	A	1.0	1.5	1.5	1.5	2.0	2.5	3.5
													B	0	0.75	0.75	1.5	2.0	2.5	3.0
													C	0.75	1.5	1.5	2.0	2.0	2.5	3.5
29	9.3	27.2	97.3	66.8	13.6	5.0	$3\frac{1}{4}$	6.1	5.98	0.47	2	2	A	0	0	0	0.5	1.25	1.25	1.5
													B	0	0	0	0.5	1.0	1.0	1.25
													C	0	0	0	0.25	0.5	0.5	0.5
46	21.4	27.2	97.3	68.8	13.8	2.0	$3\frac{1}{8}$	4.1	6.06	0.48	2	1	A	0	0.5	1.0	1.25	1.5	2.0	3.0
													B	0	0.25	0.5	1.0	1.5	2.0	3.0
													C	0	0.5	0.5	1.0	1.5	2.0	3.0
47	21.4	27.2	97.3	68.8	13.8	2.0	$3\frac{1}{8}$	4.2	6.05	0.48	2	2	A	0	0.5	0.5	0.5	0.5	0.5	0.75
													B	0	0	0	0	0	0	0
													C	0	0	0	0	0	0	0.25

(mixes 35A and 34A) are much less affected by the different curing procedures, but of course they show much greater durability than non-air-entrained concrete.

The rapid gain in weight of the dry cured specimens in the early stages of freezing and thawing is due to absorption of water by the dry concrete and not to deterioration caused by freezing and thawing. Because of the difficulty of interpreting the part played by absorption, the change in weight of the specimens is considered the least reliable of the three methods of measuring durability.

Figures 11 and 12 show the effect of different testing procedures on concretes cured by procedures 3 and 4, respectively. In both cases, the much more severe effect of test procedure 1 is demonstrated. This is noticeable in the case of air-entrained concrete as well as plain concrete, although the low durability of mix 41A as compared with mix 35A is probably due partly to the lower air content.

The effect of silicone treatment on the freeze-thaw durability of normal concretes is shown in Figures 1 to 8. Each combination of the different curing and testing procedures is shown in a separate figure.

In general, the results demonstrate the close similarity between the freeze-thaw durability of silicone-treated and untreated concrete. In many cases, there is a slight but quite definite improvement in the durability of the silicone-treated non-air-entrained concrete, but this is much less noticeable with air-entrained concrete; for example, mix 15 vs 17 in Figure 4, and mix 32 vs 34 in Figure 5.

The different curing and testing procedures resulted in no significant difference in the effectiveness of the silicone coating, although the results indicated a possible slight advantage (for the silicone) in a period of dry curing (curing procedures 2 and 4) and in the use of the less severe test procedure of freezing in air and thawing in water. Similarly, the use of low air contents in air-entrained concrete (3 to 4%) did not increase the beneficial effect of the silicone to any appreciable extent; in fact, this con-

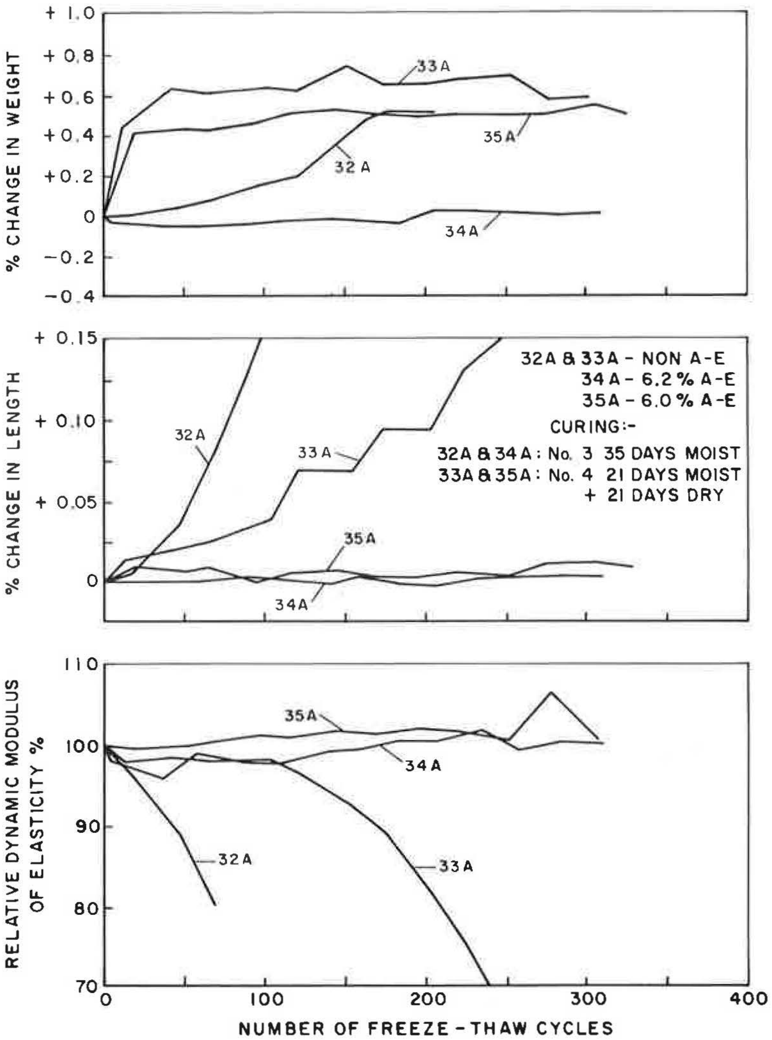


Figure 10. Effect of different curing procedures on untreated air-entrained and non-air-entrained concrete, freeze in air and thaw in water.

crete was only slightly less resistant to freezing and thawing than normal air-entrained concrete tested under similar conditions (mixes 30, 31, 38, and 39 in Figs. 5, 6, 7, and 8, respectively).

In one case (mix 33, Fig. 6) untreated non-air-entrained concrete showed markedly better durability than silicone-treated specimens of the same concrete. In this case, the concrete was cured moist for 21 days followed by 21 days dry curing (curing procedure 4) and tested by freezing in air and thawing in water (testing procedure 2). No explanation can be found for this behavior.

To demonstrate the difference that may be expected between untreated specimens and specimens that have been treated with silicones, beams from mixes 15 and 17 after completion of freeze-thaw testing are shown in Figures 16 and 17 with supplemental data given in Table 6.

A short series of tests were made with specimens made with a coarse aggregate containing a high percentage of chert which normally breaks down very rapidly when subjected to freeze-thaw testing. The results of these tests are shown in Figure 9.

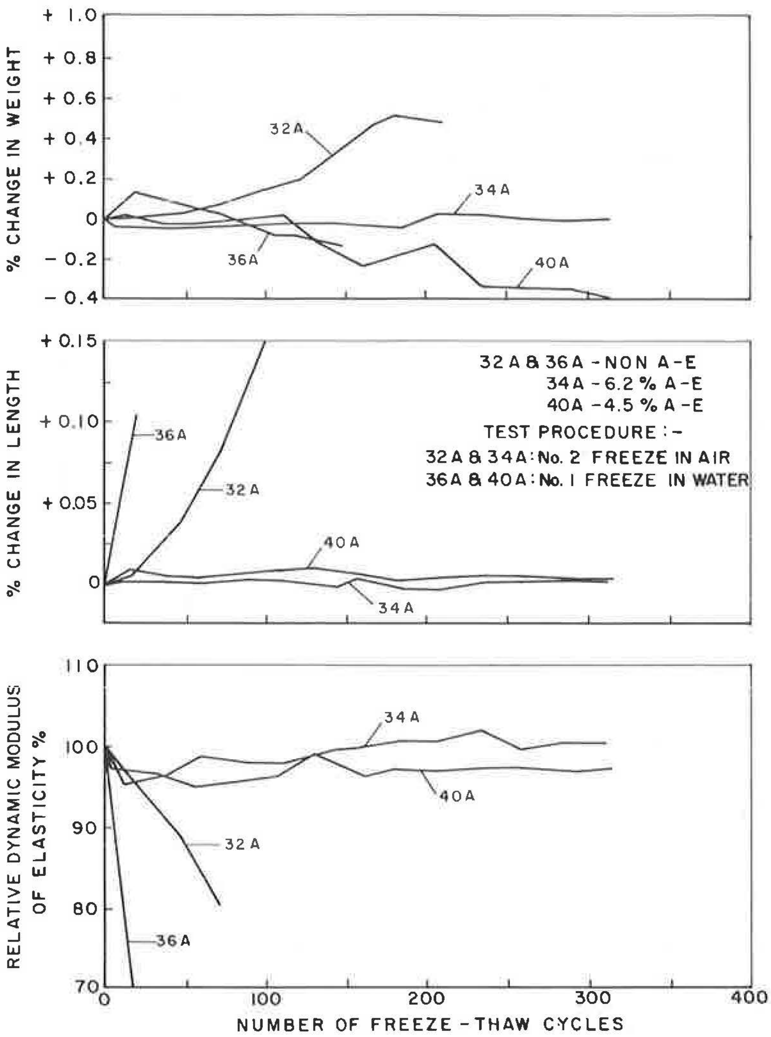


Figure 11. Effect of different testing procedures on untreated air-entrained and non-air-entrained concrete, 35 days moist.

All specimens moist cured for 35 days before testing gave similar results, with the silicone only having a slight beneficial effect. The silicone treatment gave a substantial improvement in the durability of specimens cured moist for 21 days followed by 21 days followed by 21 days of dry curing before beginning the test, the durability factor having increased by about 13 percent from 64.4 to 77.3 and 77.5 percent for the two different treatments. It appears that the silicone was relatively successful in preventing the penetration of water through the durable surface formed by the air-entrained mortar, but the improvement is not sufficient to warrant field use of this material, because experience has shown that the durability factor of over 90 percent is normally required for concrete to perform well under field conditions.

Scaling Tests

The results of the scaling tests are shown in Table 5 and in Figures 14 and 15. As with the freeze-thaw tests, a number of different curing and testing procedures were

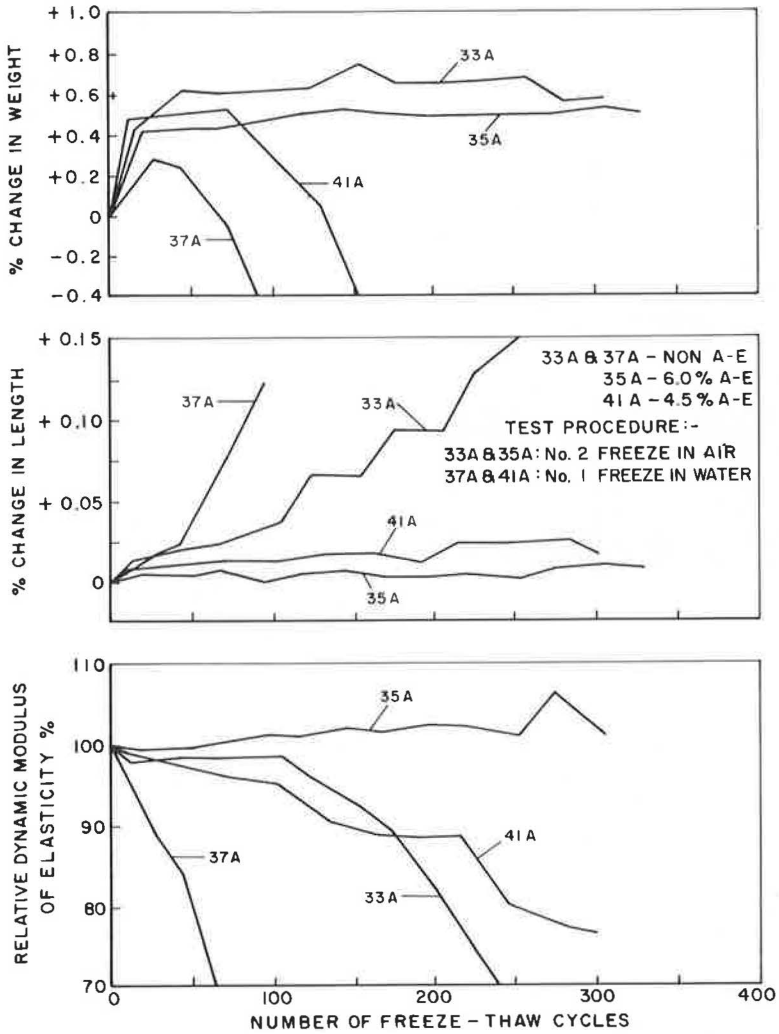


Figure 12. Effect of different testing procedures on untreated air-entrained and non-air-entrained concrete, 21 days moist + 21 days dry.

used. The slight difference in the curing procedures had little effect on the result except that the slabs that had been covered with water for three days before starting to test tended to scale more rapidly in the early stages. The two different testing procedures used had a great effect on the rate of scaling. Testing procedure 1 (freezing with the salt solution on the surface of the slab) gave the most severe condition. Scaling was much less rapid when the salt solution was removed before freezing (testing procedure 2); it may be assumed that this procedure gave a large proportion of the moisture in the surface time to evaporate before freezing started. This effect is in general agreement with the findings of Verbeck and Klieger (2).

The figures show that in most conditions the silicone coat provides only a slight beneficial effect or none at all. However, with non-air-entrained concrete subjected to the severe conditions of testing procedure 1, there was a distinct improvement in scaling resistance of silicone-coated concrete compared with untreated specimens of the same concrete. This was confirmed for both curing procedures, though the rate of scaling was more rapid when the slab had been covered with water for three days bef

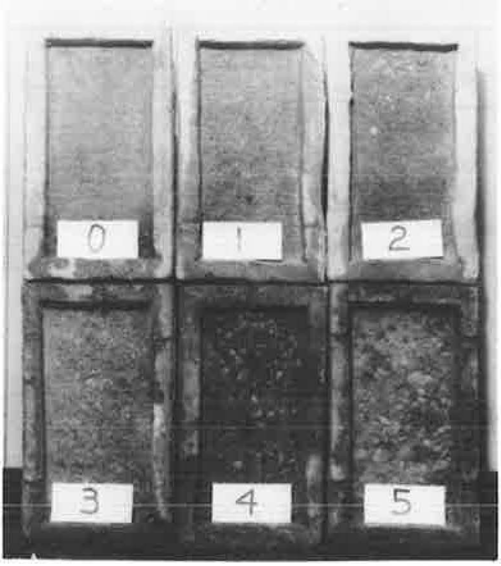


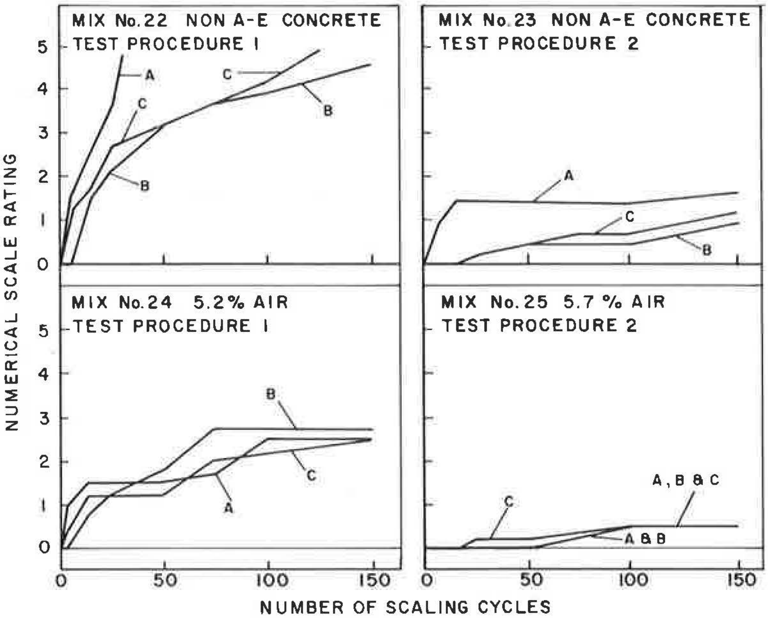
Figure 13. Standard slabs rated from 0 to 5.

TABLE 6

SILICONE TREATMENT AND NUMBER OF FREEZE-THAW CYCLES FOR MIXES 15 AND 17

Mix	Silicone Treatment	No. of Freeze-Thaw Cycles
15A	None	151
15B	1	181
15C	2	151
17A	None	495
17B	1	495
17C	2	495

starting to test. This, together with the less severe scaling resulting from testing procedure 2, indicates the advantages of allowing a drying period after the completion of curing, before applying de-icing

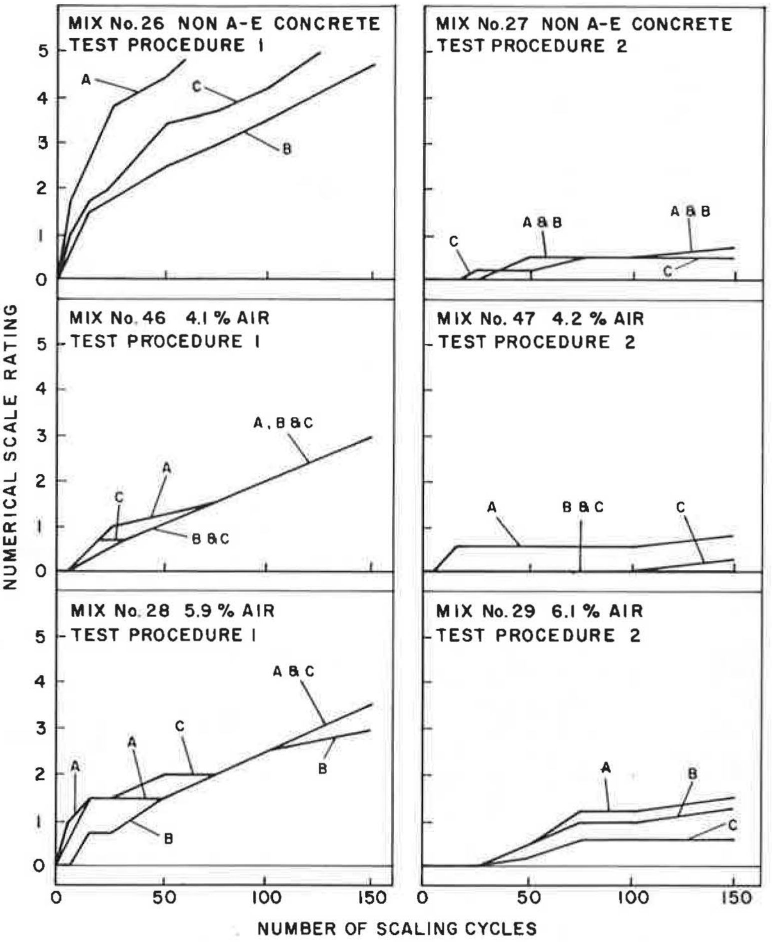


NOTES: SILICONE TREATMENT AT 28 DAYS

A - NO TREATMENT
B - SILICONE I
C - SILICONE 2

TEST PROCEDURE I - FREEZING WITH DE-ICE SOLUTION ON SLAB.
TEST PROCEDURE 2 - FREEZING WITH SLAB SURFACE DAMP.

Figure 14. Results of scaling tests, 14 days moist + 18 days dry + 3 days water covered.



NOTE : FOR DETAILS OF SILICONE TREATMENT AND TEST PROCEDURES SEE FIG. 14

Figure 15. Results of scaling tests, 14 days moist + 21 days dry.

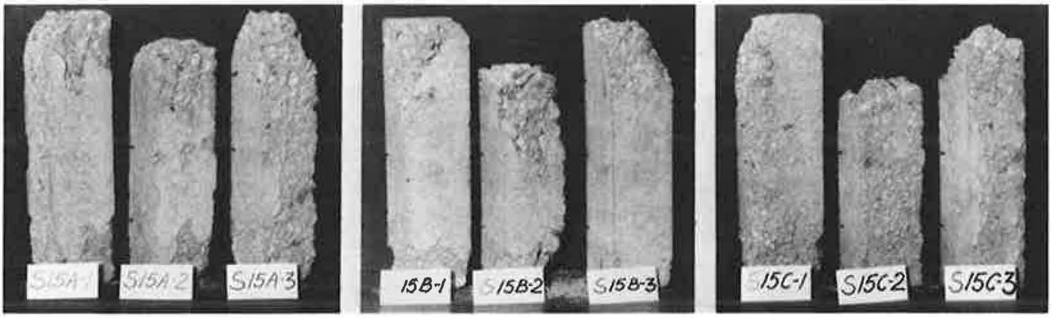


Figure 16. Non-air-entrained specimens (mix 15) after testing, 21 days moist + 14 days dry, freeze in air and thaw in water.

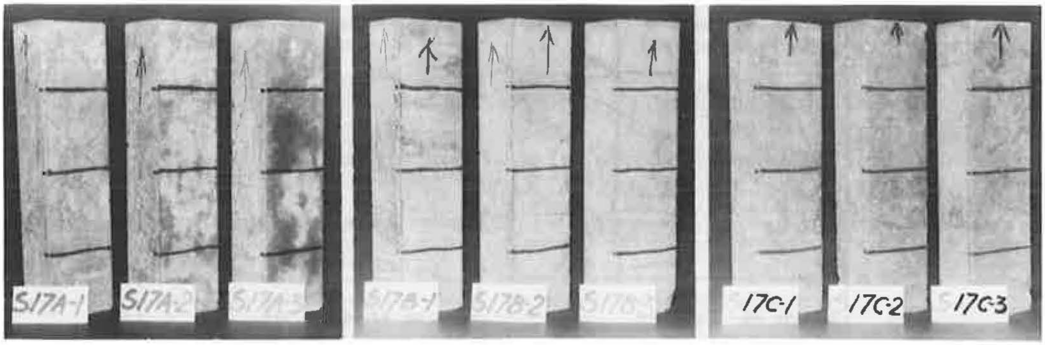


Figure 17. Five percent air-entrained specimens (mix 17) after testing, 21 days moist + 14 days dry, freeze in air and thaw in water.

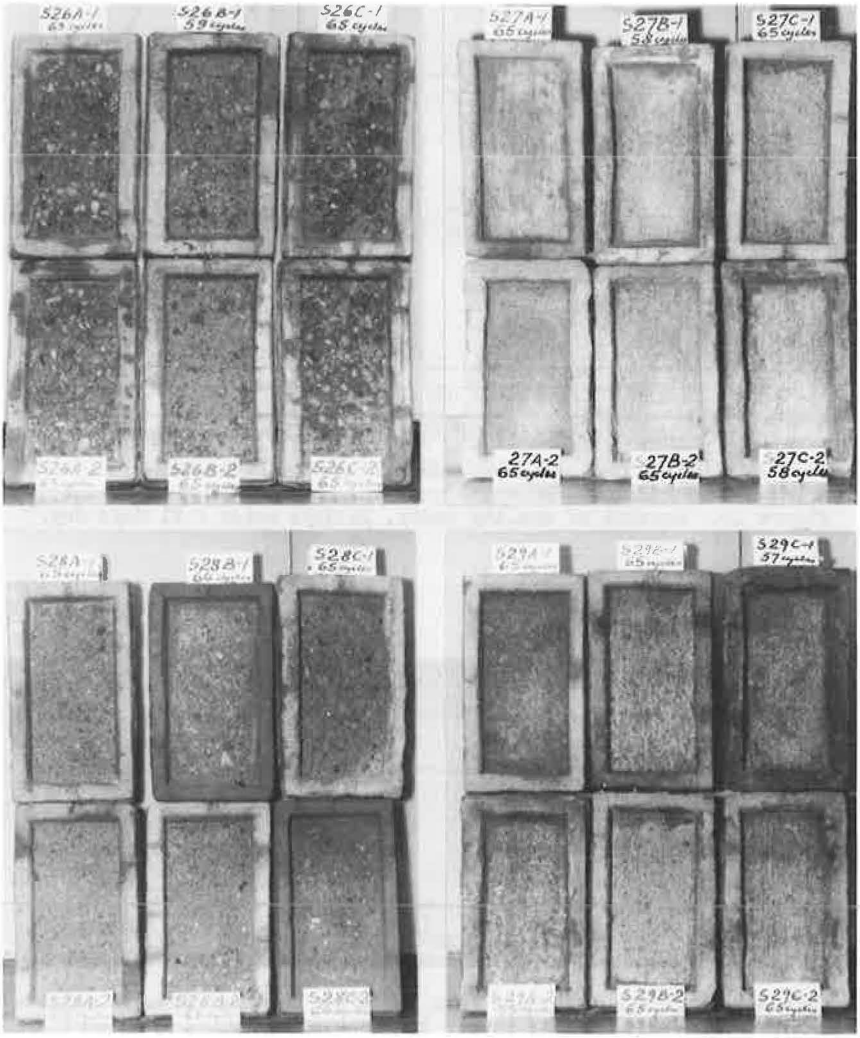


Figure 18. Specimens from mixes 26 through 29 after testing.

salts. Results of scaling tests on mixes 46 and 47 (Fig. 15) indicate that the effectiveness of the silicone coat is not increased when the concrete has a lower than normal air content (4.1 and 4.2%).

Figure 18 shows slabs from mixes 26, 27, 28, and 29 which had been subjected to between 55 and 65 cycles of the scaling test. The more severe scaling of the slabs from mix 26 is noteworthy, and the difference between the silicone-treated slabs (26B and 26C) and the untreated slabs (26A) can be seen. At this time, slabs 26A had reached a scale rating of 5.

The silicone coat on non-air-entrained concrete formed a relatively resistant surface crust, but once this crust had been broken through, severe scaling would spread rapidly across the whole slab. The early stages of this condition can be seen on slabs 26B-1 and 26B-2 on which there are a few deeply-scaled spots. On slabs 26C-1 and 26C-2, the condition is further advanced, much of the surface being deeply scaled.

CONCLUSIONS

Laboratory tests have the advantage of giving a direct comparison of differently-treated specimens under closely-controlled conditions which cannot be duplicated in the field, but the question arises as to the extent to which the test procedures adopted for the laboratory tests actually simulate conditions that may occur in the field. Therefore, it is obvious that the results of laboratory tests represent the performance of the materials under the conditions of test only; however, it is usually possible to interpret test results in the light of previous field experience. For instance, Klieger (3) states that, for the particular test procedure he used, extended laboratory experience shows that a scale rating of 1 at 100 cycles of test indicates excellent resistance to surface scaling under field conditions. For the more severe conditions of scale testing procedure 1, a scale rating of 2.5 at 100 cycles may be taken to indicate excellent performance under field conditions. Similarly, in the freeze-thaw tests a durability factor greater than 90 will in general indicate excellent resistance to freezing and thawing in the field.

It is apparent from the results that (a) adequate scaling and freeze-thaw resistance can be obtained by the use of proper air entrainment and (b) the use of silicone on non-air-entrained concrete does not increase its resistance to an acceptable level.

Smith (4) has reported Ontario's field experience with silicones, and concluded that they impart no lasting durability or scaling resistance to inadequately air-entrained concrete.

The results of the laboratory tests taken in conjunction with field experience indicate that the general use of silicone as a protective coating for concrete cannot be justified.

ACKNOWLEDGMENTS

This work has been carried out by the staff of the Materials and Research Division of the Department of Highways, Ontario, under the supervision of A. Rutka, Materials and Research Engineer, and J. Casey, Principal Testing Engineer.

The testing program was initiated by P. Smith, Senior Materials Engineer (Concrete), who together with J. Ryell and B. Chojnacki, made valuable contributions to the work.

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2. Verbeck, G. J., and Klieger, P., "Studies of 'Salt' Scaling of Concrete." HRB Bull. 150, 1-13 (1957).
3. Klieger, P., "Curing Requirements for Scale Resistance of Concrete." HRB Bull. 150, 18-31 (1957).
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Appendix

ROUTINE TESTS ON MATERIALS

Cement

In all tests, the cement used was normal portland cement supplied from a plant in Ontario. Routine tests on samples of this cement were made in accordance with CSA Specification A5-1951, except that determinations of sodium and potassium oxides were made in accordance with ASTM C114-58T. Results are given in Table 7.

TABLE 7

PHYSICAL AND CHEMICAL ANALYSIS OF CEMENT USED

Property	Sample			
Date Sampled	12 Nov. '58	23 Feb. '59	22 Apr. '59	6 July '59
Normal consistency (%)	24.5	23.5	24.0	24.0
Fineness (ret. on No. 200)(%)	3.6	4.6	2.0	2.0
Autoclave expansion (%)	0.03	0.04	0.05	0.25
Setting time (Vicat):				
Initial (hr:min)	2:45	3:25	2:40	2:45
Final (hr:min)	4:15	5:20	4:40	4:00
Compressive strength (psi):				
3 days	2,430	2,390	2,220	2,230
7 days	3,220	2,970	2,830	2,880
28 days	4,630	4,180	4,350	4,150
Loss on ignition (%)	1.56	-	-	1.77
Insoluble residue (%)	0.16	-	0.20	0.15
Sulfur trioxide (%)	2.16	-	2.37	2.25
Magnesia M_gO (%)	3.05	-	3.49	3.18
K_2O (%)	-	-	0.74	0.48
Na_2O (%)	-	-	0.64	0.48

Coarse Aggregate

Two ¾-in. coarse aggregates were used from Brighton, Ont., (crushed gravel) and Hagersville, Ont., (crushed rock). Average results of tests on the coarse aggregates are given in Table 8.

TABLE 8

PROPERTIES OF AGGREGATES USED

Aggregate Type	Source	Bulk Spec. Gravity[1]	24-Hr Absorp. (% by wt.)
Coarse	Brighton	0.70	0.4
	Hagersville	2.63	1.4
Fine	Caledon	2.66	0.9
	Paris	2.69	1.2

Petrographic analysis of the aggregates showed that the Brighton gravel contained approximately 70 percent limestone, 15 percent igneous rock, and 15 percent miscellaneous metamorphics and other materials. The Hagersville material contained approximately 52 percent chert, 42 percent limestone and 6 percent sandstone and shale.

Fine Aggregate

Two natural aggregates were used from Caledon and Paris, Ont. Average results of tests on the fine aggregates are given in Table 8.

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[1] Saturated surface dry.

Silicone Influence on Concrete Resistance to Freeze-Thaw and De-Icer Damage

PAUL KLIEGER, and WILLIAM PERENCHIO, respectively, Manager, Field Research Section, and Associate Research Engineer, Applied Research Section, Research and Development Laboratories, Portland Cement Association, Skokie, Ill.

This paper presents the results of a comprehensive laboratory study on the effect of various silicones, used as surface treatment or as integral admixture, on the resistance of concrete to freezing and thawing and de-icer scaling. Various types of non-air-entrained and air concretes were used.

Results indicate that the surface silicone treatments resulted in lower resistance to freezing and thawing and to de-icer scaling, particularly for the non-air-entrained concretes and the concretes with an inadequate amount of intentionally entrained air. Although applications of silicone surface treatments reduced the initial rate of absorption of water, on continued immersion for periods ranging from 7 to 14 days, the total absorptions for treated and untreated concretes were essentially identical.

These studies indicate that the use of silicones for treatment of horizontal concrete surfaces such as pavement slabs or bridge decks may be detrimental rather than beneficial with regard to resistance to freezing and thawing and de-icer scaling. The most effective means for insuring such durability was to provide an adequate amount and character of entrained air in a concrete of relatively low water-cement ratio.

Silicone as an integral admixture appeared of little benefit in the performance of the non-air-entrained concretes. Vertical surfaces of air-entrained concretes were treated with silicones and then subjected to freezing in air and thawing in air with intermittent water spraying. These showed a reduced tendency to wet; however, both treated and untreated vertical surfaces showed excellent resistance to this type of exposure.

• THE USE of chemical de-icers on pavements, bridge decks, and similar elements has resulted in a marked contrast between the performance of concretes containing intentionally entrained air adequate in amount and character and the performance of those without intentionally entrained air. In the absence of entrained air, the use of chemical de-icers will result in a progressive surface deterioration (scaling). Laboratory and field studies and field performance records have clearly demonstrated that surface scaling caused by chemical de-icers can be eliminated by using intentionally entrained air and adhering to other requirements for quality concrete.

In those cases where entrained air had not been provided, or the amount provided was inadequate, the use of silicone surface treatments has been suggested to avoid the development of surface scaling (1, 2).

This study was started in 1958 to evaluate the effectiveness of surface treatment by silicone solutions with respect to both de-icer scaling and resistance to freezing and thawing in the presence of water.

Paper sponsored by Committee on Effect of Ice Control.

TABLE 1

OXIDE AND COMPOUND COMPOSITION OF TYPE I BLEND,[a] LOT 19741

Component	% by Wt.
Major:	
SiO_2	20.97
Al_2O_3	5.78
Fe_2O_3	2.92
Total CaO	62.96
MgO	2.60
SO_3	2.37
Ignition loss	1.28
Minor:	
Mn_2O_3	0.26
Free CaO	0.97
Insoluble residue	0.20
Alkali:	
Na_2O	0.22
K_2O	0.63
Total as Na_2O	0.63
Calculated potential composition:	
C_3S	43.2
C_2S	27.6
C_3A	10.4
C_4AF	8.9
$CaSO_4$	4.0
Free CaO	0.97

[a] A blend of equal parts by weight of four Type I cements; chemical analyses made in accordance with ASTM C114-58T; correction for free CaO made for potential compound composition calculation.

TEST PROGRAM

Surface scaling tests and freezing and thawing tests were conducted in the laboratory on both non-air-entrained and air-entrained concretes. Two water-cement ratios were used— one typical of high-quality paving concrete, the other considerably higher. Companion specimens were given surface treatments of water silicone solutions and mineral solvent silicone solutions, each at two concentrations of silicone solids. Tests on untreated specimens and on specimens treated with boiled linseed oil were included.

Specimens were prepared and treated for exposure outdoors, adjacent to the PCA Laboratories at Skokie, Ill. These were subjected to applications of de-icer during the winter months to melt snow and ice accumulating on their surfaces.

The effectiveness of the silicone treatment on vertical, exposed concrete surfaces subjected to freezing and thawing both in the laboratory and outdoors was also studied. In addition, a water silicone solution was used in different concentrations as an integral admixture to evaluate the effect of such an addition on durability.

Materials

The cement used in these tests was a blend prepared from four different brands of Type I cement purchased in the Chicago area. Tables 1 and 2 give the chemical composition, calculated potential compound composition, and the results of various physical tests of the cement blend and of pastes and mortars made with this cement. A natural sand from Elgin, Ill., was used as the fine aggregate. A crushed gravel from Eau Claire, Wis., typical of sound, durable coarse aggregate commonly used in concrete pavement construction, was used as the coarse aggregate in these tests. Table 3 gives data on their grading, specific gravity, and absorption properties.

Aggregates were air dried and screened into various size fractions—six sizes for the fine aggregate and three sizes for the coarse aggregate. During batching, the sizes were recombined to yield the gradings given in Table 3. Aggregates were weighed in the air-dried condition (moisture content known) and, 18 to 20 hr before use, inundated with a known amount of water. Before mixing, excess water was drawn off and weighed to permit calculating the net water-cement ratios.

For those mixes containing intentionally entrained air, neutralized Vinsol resin solution was added at the mixer as the air-entraining admixture.

Three different silicone solutions were used:

1. Brand A.—A mineral spirit (petroleum thinner) solution of silicone used at two concentrations of silicone solids (2% and 5% by weight).
2. Brand B.—A mineral spirit solution of silicone used at two concentrations of silicone solids (3% and 5% by weight).
3. Brand C.—A water solution of silicones used at two concentrations of silicone solids (3% and 5% by weight).

TABLE 2

PHYSICAL TESTS[a] OF CEMENT BLEND AND MORTARS—LOT 19741

Test Type	Property	Value
Cement	Specific surface (cm^2/g):	
	Wagner	1,725
	Blaine	3,360
	Passing No. 325 mesh (%)	92.5
	Specific gravity	3.16
	Normal consistency (%)	26.0
	Time of setting, Gillmore (hr:min):	
	Initial	4:40
	Final	7:10
	Autoclave expansion (%)	0.11
	Air content, 1:4 mortar (%)	11.2
Mortar strength	Tensile (C190 briquets) (psi)	
	3 days	305
	7 days	420
	28 days	415
	Compress. (C109 cubes) (psi)	
	3 days	2,590
	7 days	3,450
	28 days	4,900

[a] Made in accordance with ASTM methods of tests current May 1959.

TABLE 3

AGGREGATE DATA

Aggregate Type	Source	Fineness Modulus	Bulk Spec. Gravity[a]	24-Hr Absorp. (% by wt.)	Grading	
					Sieve Size	% Retained
Natural sand	Elgin, Ill.	2.90	2.65	2.25	No. 4	0
					No. 8	18
					No. 16	33
					No. 30	57
					No. 50	87
					No. 100	95
Crushed gravel	Eau Claire, Wis.	---	2.69	1.33	1½-in.	0
					1-in.	---
					¾-in.	25
					⅜-in.	70
					No. 4	100
Combined	---	---	2.69	1.33	1½-in.	0
					1-in.	---
					¾-in.	50
					⅜-in.	75
					No. 4	100

[a] Saturated, surface dry.

TABLE 4

CONCRETE CHARACTERISTICS[a]

Mix No.	Cement Content (bags/cu yd)	Net W/C (gal/bag)	Slump (in.)	Net Air Content (% pressure)	28-Day Comp. Str.[b] (psi)
3	6.02	4.67	2.3	1.60	6,360
4	6.00	4.49	2.6	5.15	5,370
5	4.07	7.20	2.3	2.40	3,350
6	4.10	6.46	2.6	5.25	3,510

[a] Cement Type I laboratory blend, Lot 19741; aggregate, Elgin, Ill., sand and Eau Claire, Wis., gravel (1-in. maximum size); air-entraining admixture of neutralized Vinsol resin added at mixer to entrain 5 ± ½% air. Cylinders cured moist at 73 ± 3 F and 100% relative humidity.

[b] 6- by 12-in. cylinder.

The lower concentration of silicone solids was that recommended by the manufacturer for each of the brands.

Two coats of boiled linseed oil were applied—the first coat was 50 percent linseed oil plus 50 percent mineral spirits; the second, 100 percent boiled linseed oil.

In addition, companion specimens were treated with applications of 100 percent mineral spirits and 100 percent water, each applied in the same manner and at the same time as the silicone solutions.

The de-icer used in these tests was commercial flake calcium chloride.

Concrete Mixtures

Concretes had cement contents of 4 or 6 bags per cu yd and a slump of 2 to 3 in. Non-air-entrained and air-entrained concretes were prepared for each cement content. The air contents for the air-entrained concretes ranged from 5 to 6 percent. The maximum size of aggregate used was 1 in. for the specimens tested in the laboratory and 1½ in. for those in outdoor exposure. Data on the concretes are given in Table 4.

Fabrication of Specimens

Materials, equipment, and the mixing room were maintained at 73.4 ± 3 F. The relative humidity of the mixing room was maintained at 50 percent. Batches were mixed for 2½ min in a 1¾-cu ft open-tub mixer. For the major portion of the work, a slump test and an air content determination by the pressure method were made on three of six like batches. For each concrete mixture, six batches were prepared, two on each of three successive days. The two batches on each day comprising one round contained sufficient concrete to make ten 3- by 6- by 15-in. slabs, ten 3- by 3- by 11¼-in. prisms, and one 6- by 12-in. cylinder. Thus, for each concrete mixture 30 slabs, 30 prisms, and 3 cylinders were fabricated. All specimens were cast in watertight steel molds. Compaction was attained by hand rodding in accordance with ASTM practice. Slab surfaces were struck off and finished with a cork float. Approximately 3 hr after casting, a rich, air-entrained mortar dike was cast around the edges of the finished slab surface.

Curing Conditions and Surface Treatment

After 24 hr in the molds, during which time they were protected from drying by damp burlap covers, the slabs and prisms were cured in a moist room at 73.4 ± 3 F and 100 percent relative humidity for 13 days, followed by 14 days in air at the same temperature and 50 percent relative humidity. Slabs were then stored in air for an additional three days with a ¼-in. layer of water on the top surface. Prisms were immersed in water during this 3-day period. Cylinders were cured continuously moist until the age of 28 days.

On the seventh day of the 14-day drying period, those slabs and prisms designated for surface treatment were given applications by flooding the surface and brushing (Table 5). All materials and specimens were at 73 F during treatment.

Testing Procedure

The 6-by 12-in. cylinders were tested in compression at the age of 28 days.

The slab specimens were used to evaluate the resistance of the surface to de-icer scaling. The top surface (6 by 15 in.) was covered with a ¼-in. layer of water retained by the mortar dikes. This water and the slab were frozen in a room maintained at 0 F and thawed at approximately 70 F. At the start of the thawing portion of the cycle, flake calcium chloride was applied to the ice in an amount equivalent to 2.4 lb per sq yd of surface area, the amount used in all earlier standard laboratory tests of resistance to de-icer scaling. The slabs were subjected to one cycle of this procedure each day of the week. Visual examination at regular periods determined the amount of scaling, and numerical ratings were assigned as follows:

TABLE 5

SURFACE TREATMENTS

Surface Treatment			Specimen No. in Each Round
Type	% Solids	Sq Ft per Gal	
None	---	---	1
Silicone A	2	100	2
	5	100	3
Silicone B	3	100	4
	5	100	5
Silicone C	3	100	6
	5	100	7
Linseed oil	---	450[a]	8
		600[b]	8
Mineral spirits	---	100	9
Water	---	100	10

[a] First coat: $\frac{1}{2}$ linseed oil + $\frac{1}{2}$ mineral spirits.
[b] Second coat: 100% linseed oil.

TABLE 6

INFLUENCE OF SURFACE TREATMENT ON ABSORPTION OF CONCRETES[a]

Cement (bags per cu yd)	Surface Treatment			Absorption (% by weight)									
				Non-Air-Entrained Cement					Air-Entrained Cement				
	Type	Solvent	% Solids	5 Min	6 Hr	1 Day	2 Days	3 Days	5 Min	6 Hr	1 Day	2 Days	3 Days
6	None	---	---	0.3	0.8	1.0	1.2	1.2	0.4	1.0	1.2	1.3	1.4
	Silicone A	Mineral	2	0	0.4	0.7	0.9	0.1	0	0.4	0.7	0.9	1.0
			5	0	0.2	0.4	0.6	0.7	0	0.2	0.5	0.6	0.7
	Silicone B	Mineral	3	0	0.2	0.6	0.8	0.9	0	0.3	0.7	0.9	1.0
			5	0	0.1	0.4	0.6	0.7	0	0.2	0.4	0.6	0.8
	Silicone	Water	3	0	0.3	0.7	0.9	1.1	0	0.4	0.7	1.0	1.2
			5	0	0.2	0.5	0.8	1.0	0	0.3	0.6	0.9	1.1
	Linseed oil[b]	---	---	0	0.2	0.4	0.4	0.5	0	0.2	0.4	0.5	0.6
	Mineral spirits[c]	---	---	0.3	0.8	1.0	1.2	1.2	0.3	0.9	1.1	1.2	1.3
	Water[c]	---	---	0.3	0.8	1.0	1.2	1.2	0.3	0.9	1.1	1.3	1.3
4	None	---	---	0.5	1.8	2.3	2.5	2.6	0.6	1.6	2.1	2.3	2.3
	Silicone A	Mineral	2	0.1	0.7	1.3	1.6	1.8	0.1	0.8	1.4	1.7	1.9
			5	0.1	0.3	0.6	0.9	1.0	0	0.4	0.7	1.0	1.2
	Silicone B	Mineral	3	0.1	0.4	0.9	1.2	1.5	0	0.5	1.0	1.3	1.6
			5	0.1	0.3	0.6	0.9	1.2	0	0.3	0.7	1.0	1.2
	Silicone C	Water	3	0.1	0.4	0.9	1.4	1.9	0	0.4	1.0	1.6	2.1
			5	0.1	0.4	0.9	1.4	1.9	0.1	0.4	1.0	1.6	2.0
	Linseed oil[b]	---	---	0.2	0.6	1.1	1.4	1.6	0.1	0.5	1.0	1.2	1.4
	Mineral spirits[c]	---	---	0.5	1.8	2.3	2.4	2.5	0.4	1.6	2.0	2.2	2.3
	Water[c]	---	---	0.6	1.8	2.2	2.4	2.5	0.5	1.7	2.0	2.2	2.3

[a] 3-day immersion period.
[b] Two coats.
[c] 100%; same coverage rates as for silicone solutions.

TABLE 7

INFLUENCE OF SURFACE TREATMENT ON ABSORPTION OF CONCRETES[a]

Cement		Surface Treatment			Absorption (% by weight)							
Bags per Cu Yd	Type	Silicone	Solvent	% Solids	5 Min	6 Hr	1 Day	3 Days	7 Days	14 Days	4 Weeks	42 Weeks
6	Non-air-entr.	None	---	---	0.4	1.0	1.2	1.3	1.4	1.5	1.6	1.8
		B	Mineral	3	0	0.3	0.7	1.1	1.3	1.5	1.6	1.9
				5	0	0.3	0.6	0.9	1.2	1.4	1.5	1.9
		C	Water	3	0	0.4	0.8	1.3	1.4	1.6	1.7	1.9
				5	0.1	0.3	0.7	1.2	1.4	1.5	1.7	1.9
	Air-entr.	None	---	---	0.4	1.0	1.2	1.4	1.5	1.6	1.7	2.0
		B	Mineral	3	0	0.4	0.8	1.1	1.4	1.5	1.7	2.2
				5	0	0.4	0.6	1.0	1.2	1.4	1.5	2.1
		C	Water	3	0	0.4	0.9	1.2	1.5	1.6	1.8	2.1
				5	0.1	0.4	0.8	1.2	1.4	1.6	1.8	2.2
4	Non-air-entr.	None	---	---	0.7	2.0	2.3	2.6	2.8	3.0	3.0	3.1
		B	Mineral	3	0.1	0.4	0.8	1.7	2.6	3.0	3.1	3.3
				5	0	0.3	0.7	1.4	2.4	3.0	3.1	3.4
			Water	3	0	0.5	1.3	2.6	3.1	3.2	3.2	3.4
				5	0	0.4	1.0	2.3	2.9	3.0	3.0	3.2
	Air-entr.	None	---	---	0.6	1.9	2.3	2.6	2.8	2.8	2.9	3.2
		B	Mineral	3	0	0.4	1.0	1.9	2.6	2.8	2.9	3.2
				5	0	0.3	0.7	1.5	2.4	2.6	2.8	3.1
			Water	3	0.1	0.6	1.6	2.6	2.9	3.0	3.1	3.3
				5	0.1	0.6	1.2	2.4	2.8	2.9	3.0	3.2

[a] 42-week immersion period.

0 = no scale.
1 = slight scale.
2 = slight to moderate scale.
3 = moderate scale.
4 = moderate to heavy scale.
5 = heavy scale.

The concrete prisms were used to determine the rate of absorption during the 3-day immersion period before the start of the freezing and thawing tests. The rates were determined by weighing the specimens after the following immersion periods: 0, 5, 15, and 30 min, 1, 3, 6, 24, 48, and 72 hr. At the end of the 3-day immersion period, the prisms were frozen and thawed while immersed in water. Two complete cycles of freezing and thawing were obtained each day. The minimum specimen temperature attained was approximately -10 F and the maximum was approximately +55 F. Rate of cooling was about 20 F per hr. At regular periods during the test, determinations were made of changes in length, weight, and fundamental frequency of transverse vibration (sonic modulus, ASTM C 215). This freezing and thawing test procedure produces results comparable to those obtained by the procedure outlined in ASTM C 290, "Test for Resistance of Concrete Specimens to Rapid Freezing and Thawing in Water." Changes in fundamental transverse frequency are presented as durability factors, calculated as shown in C 290 for an endpoint of 300 cycles or the number of cycles for the ratio of the square of the frequency to reach 60 percent, whichever is reached first. The larger the numerical value of DF, the greater the potential durability. Durability factors below about 65 are indicative of poor resistance to freezing and thawing under these test conditions.

RESULTS

Influence of Treatment on Absorption

Table 6 gives the absorptions of concrete prisms with and without the various surface treatments which were determined during the 3-day immersion period immediately before the start of the freezing and thawing tests. Although the surface treatments effectively reduce the absorption during the early hours of immersion, with continued

TABLE 8

INFLUENCE OF SURFACE TREATMENT ON ABSORPTION OF CONCRETES[a]

Cement		Surface Treatment			Absorption at End of Immersion Period (% by weight)								
Bags per Cu Yd	Type	Silicone	Solvent	% Solids	1st Cycle	2nd Cycle	3rd Cycle	4th Cycle	5th Cycle	6th Cycle	7th Cycle	8th Cycle	9th Cycle
6	Non-air-entr.	None	---	---	1.4	1.4	1.3	1.4	1.4	1.5	1.5	1.5	1.4
		B	Mineral	3	1.2	1.2	1.2	1.1	1.2	1.4	1.4	1.4	1.4
				5	1.2	1.1	1.1	1.0	1.0	1.4	1.4	1.4	1.4
		C	Water	3	1.4	1.4	1.4	1.3	1.3	1.5	1.4	1.4	1.4
				5	1.4	1.4	1.4	1.3	1.3	1.5	1.5	1.4	1.4
	Air-entr.	None	---	---	1.5	1.5	1.4	1.4	1.4	1.6	1.6	1.5	1.5
		B	Mineral	3	1.4	1.4	1.4	1.4	1.4	1.7	1.7	1.6	1.6
				5	1.2	1.2	1.1	1.1	1.1	1.5	1.5	1.4	1.5
		C	Water	3	1.5	1.5	1.6	1.5	1.5	1.7	1.6	1.6	1.6
				5	1.4	1.4	1.4	1.4	1.4	1.6	1.5	1.5	1.5
4	Non-air-entr.	None	---	---	2.8	2.8	2.8	2.8	2.8	3.0	3.0	3.0	3.0
		B	Mineral	3	2.5	2.6	2.4	2.5	2.6	3.0	3.1	3.1	3.2
				5	2.1	2.0	1.8	1.9	2.0	2.9	3.0	3.1	3.2
		C	Water	3	3.0	2.9	2.9	2.9	2.9	3.1	3.1	3.0	3.1
				5	3.0	2.9	3.0	3.0	3.0	3.1	3.1	3.1	3.1
	Air-entr.	None	---	---	2.6	2.6	2.6	2.6	2.6	2.9	2.9	2.9	2.9
		B	Mineral	3	2.5	2.5	2.4	2.4	2.4	2.9	2.9	2.9	3.0
				5	2.2	2.0	1.8	1.9	2.0	2.8	2.9	3.0	3.0
		C	Water	3	2.7	2.6	2.6	2.7	2.7	2.9	2.9	2.9	2.9
				5	2.8	2.8	2.8	2.8	2.8	3.0	3.0	3.0	3.0

[a] Alternate immersion and drying periods: first 5 cycles, 7 days in water followed by 7 days in air; last 4 cycles, 28 days in water followed by 28 days in air.

immersion, the absorptions approach those for the uncoated concretes. This is particularly true for the silicone solutions.

These results prompted a repetition of a portion of the tests to provide information on absorption beyond the 3-day period, because horizontal surfaces of pavements and bridge decks may be covered with water or de-icer solution for considerable periods of time during the winter. Prisms were fabricated using concretes essentially identical to the mixtures given in Table 4. Silicones B and C, each at the 3 and 5 percent silicone solids concentrations, were applied to the surfaces in the manner previously described. One set was used for determining absorption during continuous immersion for as long as 42 weeks; a duplicate set was used to determine the influence of alternate periods of immersion and drying on absorption.

Table 7 gives the absorption results for various periods up to 42 weeks of immersion. At 7 to 14 days, the absorptions are essentially equal, regardless of surface treatment and remain so until the end of the period shown.

Table 8 gives the absorptions at the end of the immersion period portion of a number of alternate cycles of wetting and drying. Absorptions at the end of each immersion period following a drying period are essentially equal, and the absorption during each of the immersion periods followed the pattern given in Table 7. During the drying periods, the rate of water loss was the same for the control and treated concretes at each cement content.

Since performing these absorption tests to evaluate the influence of immersion time, a reference (3) to similar work was found which indicated that, although there were differences in absorption initially, with continued immersion the absorption of silicone-coated and uncoated concretes was essentially identical.

Influence of Treatment on Resistance to Freezing and Thawing in Water

The durability factors for the concrete prisms frozen and thawed while immersed in water are given in Table 9. The durability factors for all the non-air-entrained concretes were low, and differences caused by either the various silicone treatments or the linseed oil application were of little practical significance. The durability factors for all the air-entrained concretes were high (none less than 95); again, there would

TABLE 9

FREEZING AND THAWING TESTS OF CONCRETES[a], DURABILITY FACTORS[b]

Surface Treatment			Durability Factor[c]			
			6 Bags per Cu Yd		4 Bags per Cu Yd	
Type	Solvent	% Solids	Non-A-E	A-E	Non-A-E	A-E
None	---	---	20	103	17	104
Silicone A	Mineral	2	12	98	10	101
		5	12	98	13	99
Silicone B	Mineral	3	13	99	13	102
		5	13	97	12	100
Silicone C	Water	3	15	98	15	99
		5	15	100	17	100
Linseed oil[d]	---	---	14	95	14	97
Mineral spirits[e]	---	---	15	100	19	103
Water[e]	---	---	18	101	28	105

[a] Specimens 3- by 3- by $11\frac{1}{4}$-in. prisms.
[b] Results are average of tests of three specimens.
[c] Based on 300 cycles or 60% relative dynamic E, whichever was reached first.
[d] Two coats.
[e] 100%, same coverage rate as for silicone solutions.

appear to be little influence of surface treatment. However, for both types of concrete, the durability factors for the surface-treated concretes were always slightly lower than for the untreated or control concretes. Those concretes treated with 100 percent mineral spirits or water can also be considered as control concretes. These treatments were added to see whether the silicone vehicle (that is, mineral spirits or water) would have any influence on the durabilities.

The expansion data in Figure 1 lead to conclusions similar to those based on durability factor. Table 10 gives the changes in weight of these concretes during the freezing and thawing tests. In general, specimens treated with silicone solutions showed greater weight loss than untreated specimens, particularly for the 4-bag mix. The linseed oil treatment, however, appeared somewhat beneficial with respect to weight loss.

It appears, therefore, that concretes frozen and thawed while immersed in water are not benefited by surface applications of silicone solutions; in fact, their use may be detrimental to the performance of non-air-entrained concretes. This applies also to the linseed oil treatment; however, this treatment did reduce weight loss during freezing and thawing.

Influence of Treatment on Resistance to De-Icer Scaling

The results of the de-icer scaling tests are given in Table 11. The non-air-entrained concrete slabs treated with silicone solutions generally reached a rating of 5 (heavy scaling) sooner than the control concretes. For the 6-bag non-air-entrained concretes, the average number of cycles for the three controls (uncoated, mineral spirits, and water) to reach a rating of 5 was 117 cycles, whereas the average for all silicone-

TABLE 10

FREEZING AND THAWING TESTS OF CONCRETES[a], WEIGHT CHANGES[b]

Surface Treatment			Weight Change (%)[c]			
			6 Bags per Cu Yd		4 Bags per Cu Yd	
Type	Solvent	% Solids	Non-A-E	A-E	Non-A-E	A-E
None	---	---	+0.2	+0.1	- 5.1	-3.4
Silicone A	Mineral	2	-0.3	-0.3	-10.9	-5.7
		5	0	-1.5	-10.7	-7.5
Silicone B	Mineral	3	-0.2	-0.2	-10.9	-4.4
		5	-0.4	-0.9	-12.2	-4.0
Silicone C	Water	3	-0.3	-0.6	- 9.2	-5.3
		5	-0.4	-0.9	- 7.5	-4.8
Linseed oil[d]	---	---	+0.9	-0.1	- 2.4	-4.8
Mineral spirits[e]	---	---	-0.3	+0.4	- 6.3	-1.5
Water[e]	---	---	-0.5	+0.3	- 4.8	-1.8

[a] Specimens 3- by 3- by $11\frac{1}{4}$-in. prisms.
[b] Results are averages of tests of three specimens.
[c] At 100 cycles for non-air-entrained concretes; at 300 cycles for air-entrained concretes.
[d] Two coats.
[e] 100%, same coverage rate as for silicone solutions.

treated specimens was 84. Similarly, for the 4-bag non-air-entrained concretes, the average for the controls was 85 cycles and for the silicone-treated specimens 60 cycles. The linseed oil-coated specimens performed better than the silicone-treated ones, particularly for the 6-bag non-air-entrained concretes which failed by general deterioration rather than by de-icer scaling.

For the air-entrained concretes, the 6-bag concretes appeared relatively unaffected by the surface treatments; that is, the resistances were all at a sufficiently high level by virtue of such qualities as adequate air entrainment and low water-cement ratio. For the 4-bag air-entrained concretes, however, the mineral spirit silicone solutions resulted in a lower resistance to de-icer scaling, with one exception at a 5 percent silicone solids concentration. The water solution of silicone, however, showed no detrimental influence. For both the 6-bag and the 4-bag air-entrained concretes the linseed oil application appeared beneficial.

The ineffectiveness of silicone treatments in providing protection for non-air-entrained concretes against damage from freezing and thawing and de-icer scaling in the field has been reported recently (4). The beneficial effect of linseed oil, a treatment in use for some time, was described recently by Finney (5).

Effect of Silicone Surface Treatment on Concrete Containing Less Than Recommended Air Content

In a series of preliminary tests, concretes having a cement content of 6 bags per cu yd were prepared using a blend of cements which entrained 2.8 percent air in the concrete (in contrast with the 1.6 percent in the non-air-entrained concrete given in Table 4). For comparison, neutralized Vinsol resin was added at the mixer to entrain

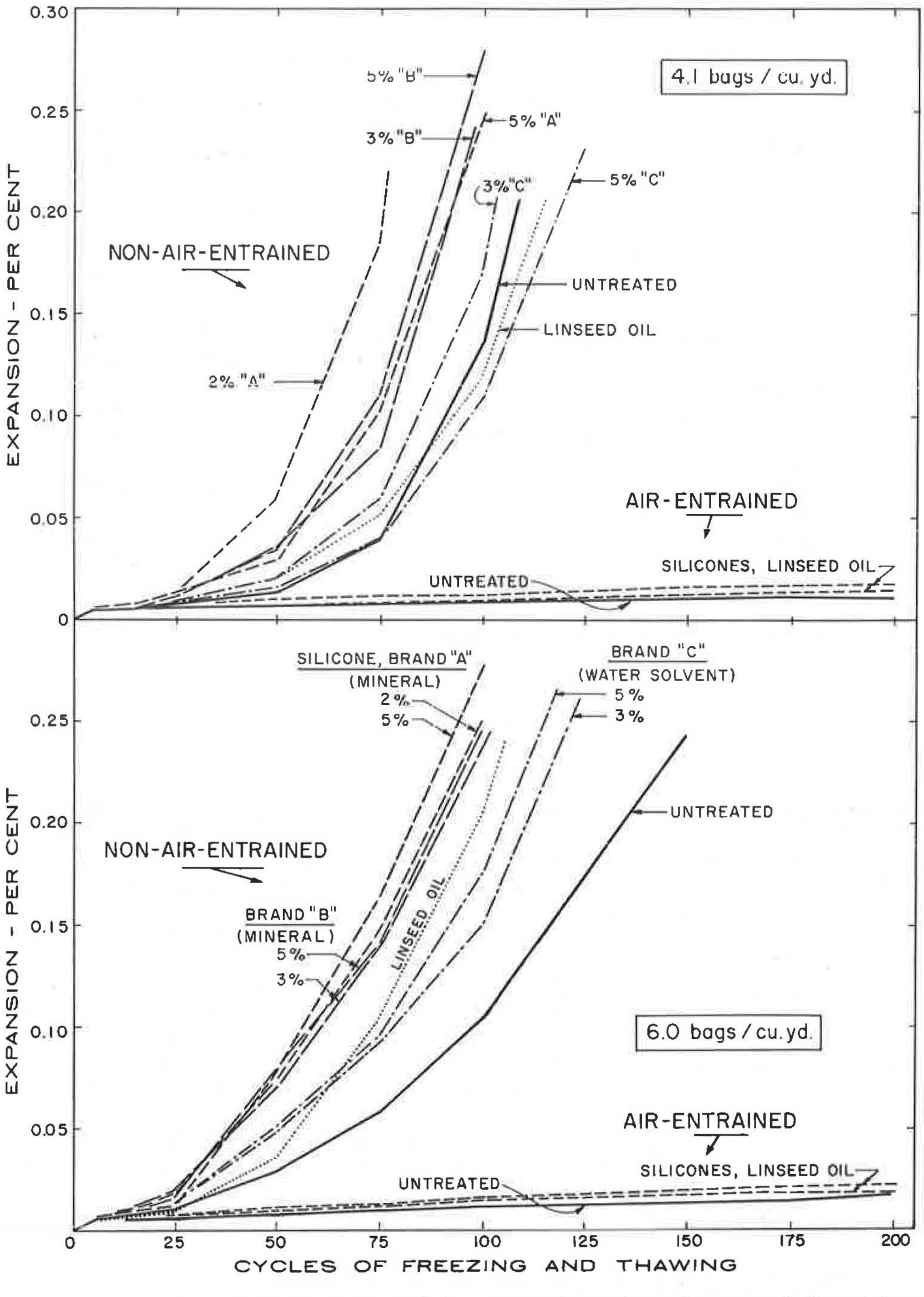

Figure 1. Expansion of 3- by 3- by $11\frac{1}{4}$-in. concrete prisms frozen and thawed immersed in water.

TABLE 11

DE-ICER SCALING TESTS[a] OF CONCRETES[b]

Surface Treatment			Scale Rating at 300 Cycles[c]			
			6 Bags per Cu Yd		4 Bags per Cu Yd	
Type	Solvent	% Solids	Non-A-E	A-E	Non-A-E	A-E
None	---	---	(115)	1	(100)	3
Silicone A	Mineral	2	(71)	1-	(55)	4-
		5	(80)	1	(73)	(238)
Silicone B	Mineral	3	(80)	1	(55)	4-
		5	(109)	1-	(66)	2+
Silicone C	Water	3	(83)	1	(58)	3
		5	(80)	1-	(55)	3
Linseed oil[d]	---	---	(122)[e]	0+	(79)	2+
Mineral spirits[f]	---	---	(130)	1-	(80)	3
Water[f]	---	---	(107)	1	(75)	3

[a] Results are averages of tests of three specimens.
[b] Specimens 3- by 6- by 15-in. prisms.
[c] Numbers in parentheses are cycles at which surface attained a rating of 5 and test was discontinued.
[d] Two coats.
[e] Surface rating was 1, but interior of slab badly cracked and disintegrating.
[f] 100%, same coverage rate as for silicones.

5.0 percent air, an adequate amount of air for this concrete. The same aggregates, fabrication procedures, curing, application of silicone treatments, and testing technique were used. The silicone solutions were the same three brands but were obtained at an earlier date.

The results of freezing and thawing and de-icer scaling tests are given in Table 12. These preliminary test results were similar in character to the more extensive data developed in the major portion of this study (Tables 9, 10, and 11, and Fig. 1). It is apparent that the surface silicone treatments were not beneficial to concrete containing some, but not an adequate, amount of intentionally entrained air. In fact, the treatments appeared to have reduced the durability, particularly the resistance to de-icer scaling. For the adequately air-entrained concrete, the effect of the treatment was slight and probably of little practical significance. Also, the 6-bag concretes in all cases showed greater resistance to de-icer scaling than the 4-bag concretes.

Effect of Silicone as an Admixture

The water silicone solution (brand C) was used as an admixture in the 6-bag per cu yd concrete at three different silicone solids concentration: 0.1, 0.2, and 0.4 percent by weight of the laboratory blend of Type I portland cements used in this study. In addition, a control non-air-entrained concrete and an air-entrained concrete were included. Data on these concretes are given in Table 13. The silicones increased the water requirements slightly and their use did not result in any intentionally entrained air, except that at 0.4 percent silicone solids a slight increase in air content and number of voids is evident.

TABLE 12

DURABILITY OF CONCRETES[a] WITH LESS THAN RECOMMENDED AMOUNTS OF INTENTIONALLY ENTRAINED AIR

Air Content (%)	C. F. (bags/ cu yd)	Net w/c (gal/bag)	Surface Treatment			Durability Factor	Expansion at 300 Cycles	Weight Change at 300 Cycles	Scale Rating
			Type	Solvent	% Solids				
2.8	6.0	4.4	None	---	---	92	0.033	-0.5	2-
			Silicone A	Mineral	2	76	0.062	-3.9	4-
					5	81	0.056	-4.4	4+
			Silicone B	Mineral	3	80	0.059	-3.4	3-
					5	81	0.051	-3.0	2+
			Silicone C	Water	3	90	0.042	-2.6	2-
					5	87	0.041	-2.0	1+
5.0	6.1	4.3	None	---	---	103	0.018	+0.2	1-
			Silicone A	Mineral	2	98	0.022	-1.5	2+
					5	98	0.025	-2.5	1-
			Silicone B	Mineral	3	100	0.021	-1.2	0+
					5	99	0.023	-1.5	1-
			Silicone C	Water	3	101	0.021	-0.1	1+
					5	101	0.020	-0.5	1-

[a] Freezing and thawing specimens 3- by 3- by $11\frac{1}{4}$-in. prisms; de-icer scaling specimens 3- by 6- by 15-in. slabs. Curing 14 days moist at 73 F and 100% relative humidity, 14 days in air at 73 F and 50% relative humidity; prisms in water and water on slab surface for 3 days thereafter. Results are averages of tests of three specimens. Concrete slump 2.4 in. for both concretes.

TABLE 13

DATA ON CONCRETES[a] CONTAINING SILICONES AS AN ADMIXTURE

Admixture	Cement Content (bag/ cu yd)	Net w/c (gal/ bag)	Slump (in.)	Net Air Content (% pressure)	Air in Hardened Concrete		
					%	Voids	
						Per In.	Per Cu In.
None	6.2	4.6	1.5	1.70	1.52	0.7	23,000
Vinsol resin	6.0	4.7	1.6	4.90	3.77	8.4	1,532,000
Silicone C[b]:							
0.1%	6.2	4.7	1.7	1.65	1.21	0.8	74,000
0.2%	6.2	4.7	1.6	1.65	0.96	0.7	23,000
0.4%	6.1	4.9	1.3	2.05	1.54	1.3	96,000

[a] Cement Type I laboratory blend, Lot 19741; aggregate, Elgin, Ill., sand and Eau Claire, Wis., gravel (1-in. maximum size); air-entraining admixture of neutralized Vinsol resin added at mixer; silicone brand C, water solution.

[b] Silicone solids as percentage of weight of cement.

TABLE 14

DURABILITY OF CONCRETES[a] WITH SILICONE ADMIXTURES

Admixture	Net Air Content (% pressure)	Water Loss (% during 14-day drying)	Absorption (% during 3 days in water)	Durability Factor[b]		Scale Rating at 300 Cycles	Expansion at 100 Cycles (%)		Weight Change at 100 Cycles (%)	
				Moist Cured	Air Dried		Moist Cured	Air Dried	Moist Cured	Air Dried
None	1.70	1.7	1.3	6	24	(156)[c]	(0.4 at 75 cy.)	0.098	(-0.4 at 75 cy.)	0
Vinsol resin	4.90	1.6	1.4	93	101	2	0.007	0.008	+0.2	+0.4
Silicone C[d]:										
0.1%	1.65	1.5	1.2	23	22	2+[e]	0.105	0.092	+0.1	+0.5
0.2%	1.65	1.5	1.2	15	12	2+[f]	0.220	0.209	-0.2	+0.2
0.4%	2.05	1.6	1.3	20	19	2+	0.076	0.108	-0.1	-0.7

[a] Freezing and thawing specimens 3- by 3- by 11$\frac{1}{4}$-in. prisms; de-icer scaling specimens 3- by 6- by 15-in. slabs. Results are average of tests of three specimens. Curing: (a) 28 days moist at 73 F and 100% relative humidity plus 3 days in water (for prisms only) and (b) 14 days moist at 73 F, 14 days at 73 F and 50% relative humidity, plus 3 days in water (for both prisms and slabs; slab surface covered with water last 3 days).

[b] Based on 60% relative dynamic E or 300 cycles, whichever was reached first.

[c] Slab disintegrated before surface reached rating of 5.

[d] Silicone solids as percentage of weight of cement.

[e] One of three slabs discontinued at 258 cycles, general cracking.

[f] One of three slabs discontinued at 151 cycles, general cracking.

Table 14 gives the results of the freezing and thawing tests of the prisms and the de-icer scaling tests of the slabs. The concretes containing intentionally entrained air show high durability factors and low expansions, whereas the control concrete and those containing silicones as an admixture show low durability factors and excessively high expansions. There is little choice between the control concrete and those containing silicones. Also, there is little difference between these concretes with respect to moisture loss on drying and absorption of water during immersion.

The de-icer scaling test results indicate that the silicone admixtures improved the resistance to surface scaling. However, general cracking and deterioration developed internally in contrast to the air-entrained concretes which showed no internal cracking or other evidence of distress.

Outdoor Exposure Specimens

Specimens prepared for outdoor storage were 18- by 24-in. slabs, 6 in. thick. Both non-air-entrained and air-entrained concretes were used. Surface treatments included the same three silicones and linseed oil. In addition, the water solution silicone was used as an admixture. Storage was outdoors at Skokie, Ill.

Table 15 gives the data on these concretes including details of curing, surface treatment, admixtures, and observations as to surface condition after two winters (1960-62) of exposure which included the use of calcium chloride as a de-icer. During these two winters, one of which was relatively mild, 15 applications of calcium chloride were made. Examination of the surfaces has disclosed few significant differences in appearance. The results of continued exposure will be of interest.

Influence of Silicones on Durability of Vertical Concrete Surfaces

Concrete blocks 8 by 12 by 12 in. in size were cast using a 6-bag per cu yd concrete containing 5.3 percent entrained air and having a slump of 2 in. These blocks were cured for 14 days moist at 73 F and 100 percent relative humidity followed by 14 days in air at 73 F and 50 percent relative humidity. After 7 days in air (21 days old), one of the 12- by 12-in. faces which was cast against a vertical mold surface (plastic-coated plywood) was treated with a silicone solution. Silicone B (mineral spirits) and silicone C (water solution) were both used at concentrations of 3 and 5 percent silicone solids. Control specimens were left uncoated. All but this one surface of each block were covered with a 1-in. layer of styrofoam. During test, the uncovered surface was kept vertical, thus simulating an exposed concrete architectural wall surface.

TABLE 15

OUTDOOR EXPOSURE SPECIMENS[a]

Concrete Type	Surface Treatment			Cement Content (bag/ cu yd)	Net w/c (gal/ bag)	Slump (in.)	Air Content (% pressure)	Admixture	Comp. Str.[b] (psi)	Comments After Two Winters' Exposure
	Type	Solvent	% Solids							
Non-air-entr.	None	---	---	5.9	4.8	2.4	1.5	None	---	OK
	Silicone A	Mineral	2	5.9	4.8	2.2	1.5	None	5,790	Mod. paper scale
			5	5.9	4.8	1.9	1.5	None	---	Mod. paper scale
	Silicone B	Mineral	3	5.9	4.8	2.8	1.5	None	5,440	Mod. paper scale
			5	5.9	4.8	2.8	1.5	None	5,760	Slight paper scale
	Silicone C	Water	3	5.9	4.8	2.1	1.4	None	6,070	Slight paper scale
			5	5.9	4.8	2.3	1.5	None	5,480	Slight pitting
	Linseed oil[c]	---	---	5.9	4.8	2.2	1.5	None	---	Slight flaking
	None	---	---	5.9	4.6	1.9	1.5	0.1% Silicone C	6,640	OK
		---	---	5.8	4.8	1.8	2.6	0.4% Silicone C	5,960	OK
Air-entr.	None	---	---	5.9	4.5	2.3	5.7	NVX	---	OK
	Silicone A	Mineral	2	5.9	4.5	2.5	5.6	NVX	4,680	OK
			5	5.9	4.5	2.4	5.3	NVX	---	Mod. paper scale
	Silicone B	Mineral	3	5.9	4.5	3.4	6.0	NVX	4,220	Mod. paper scale
			5	5.9	4.5	2.8	6.0	NVX	4,340	Slight paper scale
	Silicone C	Water	3	5.9	4.5	2.3	5.7	NVX	4,980	OK
			5	5.9	4.5	2.7	5.9	NVX	4,540	Slight pitting
	Linseed oil[c]	---	---	5.9	4.5	2.6	5.6	NVX	---	Slight pitting
	None	---	---	5.9	4.4	2.2	5.8	NVX + 0.1% Silicone C	5,240	OK
					4.7	2.5	6.2	NVX + 0.4% Silicone C	5,220	OK

[a] Cement Type I laboratory blend, Lot 19741; specimen 18 by 24 by 6 in., placed on sandy loam with crushed rock around slab up to one-half depth, with redwood dikes around surface edges. Aggregate, Elgin, Ill., sand and Eau Claire, Wis., gravel ($1\frac{1}{2}$-in. maximum size). Curing of slabs, 7 days moist at 73 F and 100% relative humidity plus 7 days in air at 73 F and 50% relative humidity, stored outdoors at 14 days; curing of cylinders, 28 days moist. Silicone and linseed oil treatments applied at end of 7-day drying period. Neutralized Vinsol resin as air-entraining admixture (NVX) Silicone C (water solution). Exposed outdoors at Skokie, Ill.; during winters, flake $CaCl_2$ applied, as required to de-ice, to produce a 2 to 3 percent solution on thawing.

[b] Of 6- by 12-in. cylinders.

[c] Two coats.

One group of specimens (one specimen per variable) was subjected to freezing and thawing tests in the laboratory. Each uncovered vertical surface was sprayed with approximately 1 pt of water and the specimen stored for 18 hr in an air freezer maintained at 0 F. At the end of this period, the specimens were moved to the thawing room maintained at approximately 70 F, and the exposed surface was sprayed immediately with the same amount of water. After 6 hr of thawing, the cycle was repeated: spray, freeze, etc. A companion group was stored outdoors at Skokie, Ill., for natural weathering.

In the laboratory after 5 cycles of test, the untreated concrete specimen showed slight "paper" scaling and a surface that wet readily, whereas the silicone-treated surfaces showed no paper scaling and did not wet. From 5 to 350 cycles, however, no further changes occurred except for a slight infiltration of water around the edges of the silicone-treated concrete surfaces. After two winters of exposure, the outdoor specimens show essentially the same performance as the laboratory specimens.

SUMMARY AND CONCLUSIONS

This study included tests of non-air-entrained and air-entrained concretes at two different water-cement ratios. Surface treatments evaluated for their influence on resistance to freezing and thawing and de-icer scaling included silicones in mineral spirits and water and a linseed oil treatment. A water solution of silicone was used in some of the tests as an admixture. The major portion of the work was performed in the laboratory. Outdoor exposure tests were included, but the time elapsed has been insufficient to develop conclusive results.

Based on these tests, the following comments and conclusions appear warranted:

1. Although applications of silicone solutions to concrete surfaces reduced the initial rate of water absorption, on continued immersion for periods of 7 to 14 days the total absorption of treated and untreated concretes were essentially identical.
2. Surface applications of linseed oil reduced the initial rate of absorption of water, and the 3-day absorption was significantly lower than for the silicone-treated concretes.
3. Non-air-entrained concretes frozen and thawed while immersed in water showed

poor durabilities. Durabilities were consistently lower with concretes surface-treated with silicones than with untreated ones. This was true for all three criteria of durability used; that is, durability factor, expansion, and weight loss. Although the linseed oil treatment was no more effective for this exposure, weight loss was no greater for concretes so treated than for the control concretes, in contrast with those treated with silicones.

Air-entrained concretes showed high durabilities, and there was no significant influence of any of the surface treatments on these durabilities.

4. Non-air-entrained concretes frozen and thawed and subjected to the use of calcium chloride as a de-icer showed low resistance to surface scaling. The use of surface silicone treatments further reduced this resistance. In the richer mix, the linseed oil treatment was effective in reducing scaling but did not prevent general deterioration typical of non-air-entrained concrete.

Air-entrained concretes having a cement content of 6 bags per cu yd showed excellent resistance to de-icer scaling, and there was no significant influence of the surface treatments on this resistance. The 4-bag per cu yd air-entrained concretes, however, showed significantly less resistance than the 6-bag concretes, and the silicone surface treatments generally further reduced this resistance.

5. The effects of the silicones were essentially the same for both the mineral spirits solutions and the water solutions.

6. Surface applications of mineral spirits or water (both used in preparing the different silicone solutions) had no influence on the resistance to freezing and thawing or de-icer scaling.

7. Concretes containing some intentionally entrained air, but less than an adequate amount, were not benefited by surface treatment with silicones. In fact, for non-air-entrained concretes the treatments were detrimental.

8. A water solution of silicone used as an admixture did not improve the resistance of non-air-entrained concretes to freezing and thawing while immersed in water. Significant improvement in resistance to de-icer scaling was apparent for these non-air-entrained concretes; however, general cracking and deterioration caused early failure.

9. Vertical exposed surfaces of air-entrained architectural concrete showed a reduced tendency to wet if treated with surface application of silicones. The silicone treatment appeared beneficial in laboratory tests, which showed untreated surfaces to develop a light paper scale or roughening, whereas the treated surfaces showed no change.

10. It would appear that the use of silicones for treatment of horizontal concrete surfaces such as pavement slabs or bridge decks has neither beneficial nor detrimental effects when used with a typical 6-bag concrete mix containing an adequate amount of intentionally entrained air. Detrimental effects of surface treatment with silicones were noted in the 4-bag mixes with and without intentionally entrained air and in the 6-bag mix with less than the recommended amount of intentionally entrained air.

11. The most effective means of insuring resistance is to provide an adequate amount and character of entrained air in a concrete of relatively low water-cement ratio.

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Factors Affecting Freezing-and-Thawing Resistance of Chert Gravel Concrete

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A three-part investigation was made of factors affecting the freezing-and-thawing resistance of concrete containing chert gravels. Principal variables were aggregate source, particle size, curing and moisture content of concrete, and cement factor. Test results were consistent with accepted concepts of the mechanism by which concrete is damaged from freezing and thawing. The data demonstrated that those concepts have important practical significance in securing best field performance from available materials.

The tests showed that (a) reduction in the size of the chert gravel improved the resistance of concrete to freezing and thawing; (b) partial drying of the concrete before exposure greatly improved its performance; (c) once partially dried, the concrete was not easily resaturated to the point of vulnerability to freezing damage; and (d) under some combinations of saturation and exposure, increasing cement content reduced the resistance of concrete to freezing and thawing.

• DURABILITY is a prime requisite of any concrete, but it is particularly critical in highway construction where maximum return is expected from the public investment. Good performance is needed not only from standpoints of safety and utility but also because of continual exposure to the critical scrutiny of the user. Shortcomings in quality of highway construction are likely to be disconcertingly apparent.

In most areas of the country, pavements and structures must be built to resist the destructive action of freezing and thawing. Past performance in this regard has not always been good, but much improvement has been made in recent years. Air entrainment provides a high degree of protection for the cement paste and mortar phases of the concrete (4, 7) but may not overcome the effects of larger aggregate particles which undergo volume changes on freezing (11). The mechanism by which concrete is damaged by freezing has become better understood, suggesting ways by which performance can be improved (5, 7, 10, 14). The materials of concrete have been evaluated in terms of their role in durability (2, 3, 6, 8), resulting in better prediction of performance and development of methods to improve borderline materials (11, 12, 13). Finally , it is being recognized that attainment of best performance will be achieved only when environmental effects are moderated to the extent practicable by proper design and protection of the structure (8, 9). The latter approach is exemplified by proper grade alignment and subgrade drainage to eliminate excessive saturation of pavements that will be exposed to freezing.

This paper does not offer new theory on the resistance of concrete to freezing and thawing. It describes researches intended to evaluate the effects on the performance of a specific type of aggregate attainable by applying already established concepts. The aggregate was chert gravel, which is available and widely used for concrete in large areas of the middle and southern Mississippi valley. Cherts and chert gravels have been extensively studied (1, 2, 6, 10, 15). It is known that their response to freezing depends

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on their pore structure, the size of particle, the rate of freezing, their degree of saturation, and the properties of the cement matrix in which they are imbedded. The researches reported here developed information on the degree to which controllable changes in some of these factors might be expected to affect the freezing-and-thawing resistance of the concrete.

SCOPE AND OBJECTIVE

Tests were made in the Joint Research Laboratory of the National Sand and Gravel Association and National Ready Mixed Concrete Association at the University of Maryland to investigate means of developing the best performance of chert gravels in concrete exposed to freezing and thawing. The investigation involved two chert gravels from different sources and of somewhat different physical characteristics, but both with long records of successful use as concrete aggregates. Their service performance has varied somewhat, apparently depending on conditions of exposure and other factors related to the production and treatment of the concrete.

The study was conducted in three phases. The first phase provided information on the relative effects of different size fractions of the chert gravel when used to replace corresponding fractions of an aggregate composed of nearly pure quartz. In the second phase, the effects of varying degrees of drying of the concrete, with and without resaturation, were investigated. In the third phase, the effects of several combinations of factors were measured: maximum size of the chert gravel, cement factor of the concrete, and two degrees of partial drying of the test specimens.

All variables in this program have been subjects of earlier researches. The studies have involved many different investigators and, in general, have not been coordinated to permit quantitative comparisons. This investigation was intended to tie together a number of loose ends. It offers encouraging evidence that the chert gravels can yield highly durable concrete if certain relatively simple precautions are observed.

EFFECTS OF PARTICLE SIZE

Description of Tests

To evaluate the relative influence of different particle sizes on concrete durability, chert gravel lot 3701 was used as the replacement for portions of a nearly pure quartz gravel of high quality, regularly used in the laboratory as a basis for comparison. The reference concrete contained the quartz gravel graded 25 percent each of 1 to ¾ in., ¾ to ½ in., ½ to ⅜ in., and ⅜ in. to No. 4. The chert gravel was successively used to replace the 50 percent of coarse aggregate between the ½ in. and No. 4 sizes, the 50 percent between 1 and ½ in., and finally the entire quantity of coarse aggregate. As in all portions of the investigation, the coarse aggregates were saturated under vacuum and soaked for 24 hr to simulate the most adverse condition likely to be encountered in the field. Physical properties of the chert gravel are discussed in the second phase.

The fine aggregate used throughout was a nearly pure silica bank sand from Branchville, Md., having a fineness modulus of approximately 2.7. The sand was thoroughly mixed and kept moist for 24 hr before incorporation in the concrete. Cement was a laboratory stock blend of 5 brands purchased locally.

All concrete was designed to contain 6 sacks of cement per cu yd with a slump of 3 to 4 in. and an air content of approximately 5 percent, secured by use of neutralized Vinsol resin added at the time of mixing. Aggregate proportions were selected on the basis of ACI Recommended Practice 613 to produce a degree of workability suitable for placement conditions in typical structures.

The concrete was mixed by hand in 0.25-cu ft batches. Slump was measured and air content determined gravimetrically from the unit weight measured in a 0.20-cu ft container. Two 3- by 4- by 16-in. beams were molded from each batch for the freezing-and-thawing tests. Three batches were made on different days for each of the four types of concrete.

To supplement information on the effects of degree of saturation secured in other portions of the investigation, the two specimens from each batch were subjected to different curing conditions. After remaining in the molds in the standard moist room for

TABLE 1

EFFECT OF SIZE OF CHERT GRAVEL ON FREEZING-AND-THAWING RESISTANCE OF CONCRETE

Gravel (%)		Mixing Day	Cement (sacks/ cu yd)	Water (gal/ cu yd)	Slump (in.)	Air (grav.) (%)	Unit Weight (pcf)	Freezing-and-Thawing Tests			
								Cycles to 50% E		Dur. Fac., 100 Cyl.	
Quartz	Chert							Curing A[a]	Curing B[b]	Curing A[a]	Curing B[b]
100	---	B	5.88	33.6	3.4	5.8	141.3	+500[c]	+500[c]	96	90
		C	5.90	33.6	3.5	5.6	141.5	+500[c]	+500[c]	95	91
		D	5.91	33.7	3.6	5.3	142.0	+500[c]	+500[c]	96	90
		Avg.	5.90	33.6	3.5	5.6	141.6	+500[c]	+500[c]	96	90
50[d]	50[e]	A	5.89	33.6	2.9	5.7	140.0	426	+500[c]	87	91
		B	5.96	34.6	3.0	4.2	141.9	453	+500[c]	87	90
		C	5.84	34.1	3.9	6.1	138.9	465	+500[c]	90	91
		Avg.	5.90	34.1	3.3	5.3	140.3	448	+500[c]	88	91
50[e]	50[d]	A	5.89	32.9	2.6	6.0	139.9	255	+500	75	92
		B	5.91	34.1	3.2	5.2	140.7	158	+500	63	91
		C	5.88	34.1	3.9	5.7	139.8	137	+500	58	92
		Avg.	5.89	33.7	3.2	5.6	140.1	183	+500	65	92
---	100	A	5.85	34.0	3.8	5.9	138.0	40	205	20	73
		B	5.93	33.6	3.1	4.6	139.8	50	160	25	72
		C	5.89	34.4	3.9	5.3	138.9	64	172	32	79
		Avg.	5.89	34.0	3.6	5.3	139.2	51	179	26	75

[a] 7 days in moist room and saturated limewater + 4 days in 70 F air at about 50% relative humidity + 3 days re-immersed in saturated limewater.

[b] 7 days in moist room and saturated limewater + 7 days in 70 F air at about 50% relative humidity.

[c] Specimens survived over 500 cycles before tests were discontinued to make equipment space available.

[d] 1- to ½-in. sizes.

[e] ½-in. to No. 4 sizes.

the first 24 hr, all beams were stripped and immersed in saturated limewater at 73 F to the age of 7 days. Thereafter, one from each batch was cured in air at 70 F and approximately 50 percent relative humidity for 4 days followed by re-immersion in limewater for 3 days before exposure to freezing and thawing; the second specimen from each batch was cured in the 70 F air for 7 days and exposed to freezing and thawing without resoaking.

At the age of 14 days, all specimens were subjected to freezing and thawing in accordance with ASTM Designation C 291-61T, "Tentative Method of Test for Resistance of Concrete Specimens to Rapid Freezing in Air and Thawing in Water." That exposure consisted of alternate freezing in air at 0 F and thawing in water at 40 F at the rate of approximately 7 complete cycles per day. Deterioration was evaluated by the nondestructive test for dynamic modulus of elasticity (ASTM Designation C 215). Exposure of a specimen was continued until its dynamic modulus had been reduced 50 percent or until it had been exposed to at least 500 cycles, whichever occurred first.

Results

Characteristics of the concrete and results of the freezing-and-thawing tests are given in Table 1. It is apparent that the four types of concrete were essentially the same in their basic characteristics of cement factor, water content, slump, and air content. Hence, they should provide a valid indication of the effects of substituting the different sizes of chert for the nearly nondestructible quartz gravel.

For specimens partially dried but resoaked before exposure, the 50 percent substitution of chert for the 1- to ½-in. sizes of quartz reduced freezing-and-thawing resistance much more than did substitution for the ½ in. to No. 4 sizes. With chert used for the smaller size, the concrete performed excellently, withstanding an average of 448 cycles of freezing and thawing. When the larger, 1- to ½-in. sizes of chert were substituted, resistance was reduced to 183 cycles, a poorer but still creditable performance. In these resaturated concretes, use of the chert gravel as the entire coarse aggregate resulted in the concrete's withstanding only 51 cycles under the severe conditions of aggregate treatment and exposure employed.

When the concrete was allowed to air dry for a full 7 days and was not resoaked immediately before freezing, good performance was secured from all combinations. Specimens in which chert comprised 50 percent of the coarse aggregate in either the smaller or larger size range withstood over 500 cycles of exposure. The concrete with 100 percent chert gravel survived an average of 179 cycles.

The data from this portion of the investigation provide two clear-cut indications. First, the smaller sizes of chert gravel are much less susceptible to the disruptive effects of freezing than are larger sizes. Second, resistance of the concrete is greatly enhanced if it has an opportunity to dry partially before being frozen. Both of these findings are consistent with, and merely confirm, accepted concepts (5, 7, 14).

EFFECTS OF CONCRETE MOISTURE CONDITION

Description of Tests

To study in more detail the magnitude of moisture effects, comparative tests were made using two chert gravels: lot 3701, the same as in the first series, and lot 3691 from a second source. General procedures for grading and treatment of the aggregates and proportioning of the concrete were the same as in the first phase with limited exceptions. Instead of being mixed by hand, the concrete was mixed for 6 min in 1.1-cu ft batches in a small tilting mixer. Slump was measured and air content determined gravimetrically using a 0.50-cu ft container. Nine 3- by 4- by 16-in. beams were molded from each batch to be subjected to 9 different sequences of curing, partial drying, and resaturation. Two batches were mixed on different days with each of the two sources of chert gravel.

All specimens remained in the molds in the standard moist room for the first 24 hr, after which they were stripped and immersed in limewater at 73 F to the age of 28 days. They were then placed in an atmosphere of 70 F air at approximately 50 percent relative humidity and treated as follows before exposure to freezing and thawing: air dried for four different periods—3, 7, 14, and 28 days—and then immediately subjected to freezing and thawing; air dried for 28 days and then resoaked for five different periods in 73 F limewater—3, 7, 14, 28, and 91 days—before exposure. The treatment combinations can be more clearly visualized from Table 2.

Results

Characteristics of the fresh concrete are given in Table 3. The two batches made with each aggregate were very similar in basic characteristics but, for purposes of the present discussion, that is not critical because the principal comparisons are among pre-exposure curing treatments represented within each batch. The freezing-and-thawing test data are given in Table 2, and pertinent relationships bearing on their significance are shown in Figures 1 through 5.

Figures 1 and 2 show specific gravity and absorption characteristics of the two chert gravels. The curves in Figure 1 indicate rate of absorption in terms of both percentage by weight of the gravel and percentage of the amount of water absorbed under vacuum saturation. Absorption of lot 3691 chert was considerably higher than that of lot 3701. However, the difference appeared to consist of the larger pores which filled with water quickly. After about the first hour, the rate of absorption was essentially the same for the two materials. Also, as shown by the upper curves in Figure 1, the relative absorption (roughly corresponding to the degree of saturation) was similarly related to time for both aggregates.

Figure 2 shows the specific gravity distribution of the two cherts, based on sink-float separations of the vacuum-saturated aggregates in heavy liquids of varying density. Lot 3701 had considerably fewer particles in the low specific gravity range than lot 3691. For example, the latter contained approximately 35 percent of particles lighter than 2.4, as compared with only about 5 percent for the former. These relationships are consistent with the bulk specific gravity and absorption data shown in Figure 1.

TABLE 2

FREEZING-AND-THAWING TESTS OF CONCRETE

Subsequent Treatment[a] (days)		Age at Start of F-T (days)	Coarse Aggregate Lot 3691							Coarse Aggregate Lot 3701						
			Weight Loss[b] (g)					Durability Factor		Weight Loss[b] (g)					Durability Factor	
At + 70 F, 50% Rel. Hum.	At + 70 F, in Lime-water		From 28 Days to F-T Start	From F-T Start to Oven Dry	Total	Satura-tion at F-T Start (%)	Cycles of F-T to 50% E	At 100 Cycles	At 200 Cycles	From 28 Days to F-T Start	From F-T Start to Oven Dry	Total	Satura-tion at F-T Start (%)	Cycles of F-T to 50% E	At 100 Cycles	At 200 Cycles
3	0	31	114	488	602	81	6	3	2	105	420	525	80	21	10	5
7	0	35	164	429	592	72	12	6	3	147	370	517	72	110	52	28
14	0	42	215	362	577	63	22	98	57	182	316	498	64	343	101	84
28	0	56	262	324	586	55	+700[c]	102	101	218	296	514	58	578	100	95
	3	59	139	448	587	76	+700[c]	100	100	92	424	516	82	612	98	94
	7	63	116	462	578	80	+700[c]	100	99	76	424	500	85	466	94	85
	14	70	107	481	588	82	647	98	99	68	436	504	87	348	92	74
	28	84	92	488	580	84	385	94	74	60	444	504	88	262	78	58
	91	147	68	514	582	88	50	25	13	42	459	501	92	176	60	44

[a] After all specimens (3- by 4- by 16-in. beams) cured 28 days in saturated limewater.

[b] Average difference between weight of beams (having approximately 3, 150-cc volume) at 28 days and at indicated condition.

[c] Specimens survived more than 700 cycles.

TABLE 3

CHARACTERISTICS OF FRESH CONCRETE

Lot No. C.A.	Mixing Day	Cement (sacks/ cu yd)	Water (gal/ cu yd)	Slump (in.)	Air (grav.) (%)	Sand (% tot. agg.)	b/bo	Unit Weight (pcf)
3691	C	6.01	33.7	2.6	4.0	36.9	0.687	138.8
	D	5.96	34.6	2.8	4.2	36.9	0.681	138.0
	Avg.	5.98	34.2	2.7	4.1	36.9	0.684	138.4
3701	C	5.91	34.6	5.0	5.3	36.5	0.681	138.7
	D	6.00	34.5	3.2	4.2	36.5	0.691	140.5
	Avg.	5.96	34.6	4.1	4.8	36.5	0.686	139.6

Figures 1 and 2 show that the lot 3691 chert has a higher capacity for absorbing water and might be expected, therefore, to be more vulnerable than lot 3701 to freezing under highly saturated conditions. The evidence also suggests, however, that water might be expected to move more readily into and out of the pores of the former. Under certain circumstances, this might benefit the resistance to freezing for either or both of two reasons (10, 14):

1. By permitting water to escape from the aggregate, and hence reduce its degree of saturation whenever the concrete has an opportunity to dry; and
2. By facilitating the movement of water through the aggregate pores during freezing, thus reducing the likelihood of disruptive pressures developing.

Principal indications from the freezing-and-thawing tests of concrete can be seen directly from the test results in Table 3. Effects of the various drying and resaturation treatments were similar for the two gravels. When the concrete, which had been kept saturated for 28 days, was allowed to dry for only 3 days, and hence could be expected to remain highly saturated on the interior, it was destroyed in a very few cycles of freezing and thawing. As the drying period was increased, resistance improved until, after 28 days of drying, the concretes were highly durable. Resoaking for 3 days after the 28-day air-drying was not harmful, but continuation of soaking thereafter progressively reduced freezing-and-thawing resistance. However, even after 28 days of reimmersion the concretes remained highly durable, withstanding 385 cycles in the case of lot 3691, and 262 cycles for lot 3701. After 91 days of resoaking, the concrete with lot 3691 withstood only 50 cycles of freezing and thawing, but that with lot 3701 was still capable of withstanding 176 cycles, a commendable performance.

Careful records were kept of the weight changes of all specimens during curing and testing. When freezing and thawing were terminated on any specimen, it was oven dried to constant weight at approximately 225 F to provide a reasonably fixed reference for moisture conditions at other stages. The first line in each portion of Table 3 indicates the amount of water lost from a specimen between 28 days, when it was at its most highly saturated condition, and the beginning of freezing and thawing. The second line shows weight loss between the start of freezing and thawing and the oven dry condition after exposure. Thus, for the first curing condition of concrete with lot 3691, the average weight of specimens at the start of freezing and thawing was 114 g less than the 28-day weight and 488 g more than the oven dry weight. The total weight difference between 28 days and the oven dry condition was 114 plus 488 or 602 g. This sum remains reasonably constant for either gravel regardless of curing treatment of the concrete. Further, the average difference between these sums for the two gravels (77 g) is only slightly less than the difference between the vacuum-saturated absorptions of the two gravels in the amount contained in a test specimen.

Figures 3, 4, and 5 show some of the factors involved in freezing resistance of the chert gravel concretes. Figure 3 shows moisture changes of concretes during the vari-

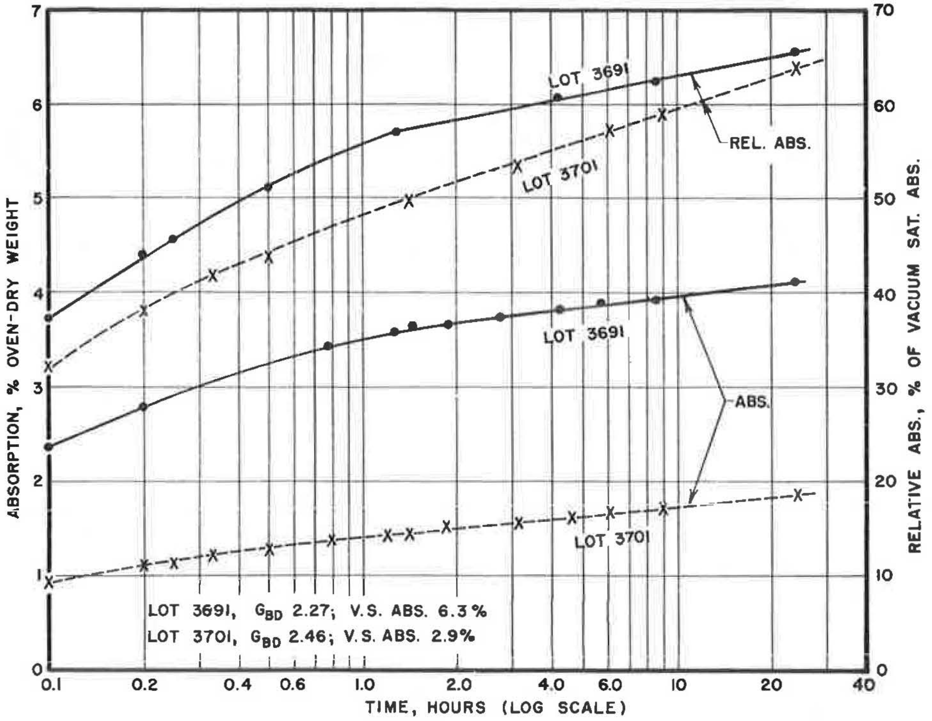

Figure 1. Absorption characteristics of chert gravels.

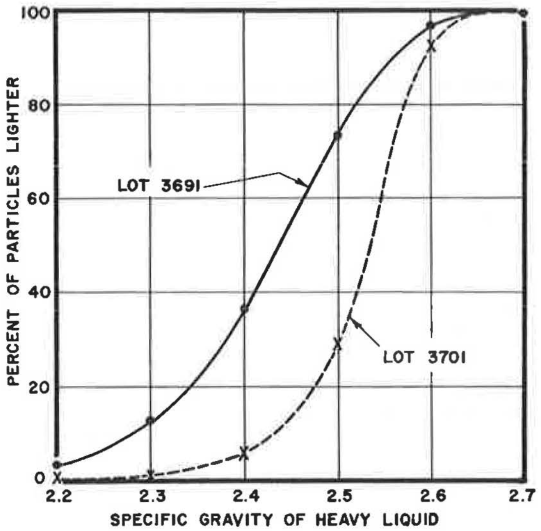

Figure 2. Specific gravity distribution of chert gravels.

ous curing treatments. As already mentioned, until the end of the initial 28-day immersion period, the difference in moisture content between concretes with the two gravels was about equal to the difference in water absorbed by the aggregates. As the concrete was dried after 28 days, more water was lost from the concrete with lot 3691 as evidenced by the reduced difference in weight. On resoaking, even after 3 months, the differential in aggregate water content was never completely restored. Without regard to what this might mean in terms of comparisons between the two gravels, it strongly suggests that the cherts are not easily resaturated once they have an opportunity to dry out reasonably well.

Support for the latter hypothesis, as well as evidence of its potential significance, is shown in Figure 4. Here, the moisture change data have been plotted in relation to the 28-day weights, when the concretes were most completely saturated. The number of cycles of freezing and thawing withstood by the various specimens has been shown at points on the curve corresponding to the times when they were removed from curing to be subjected to freezing and thawing.

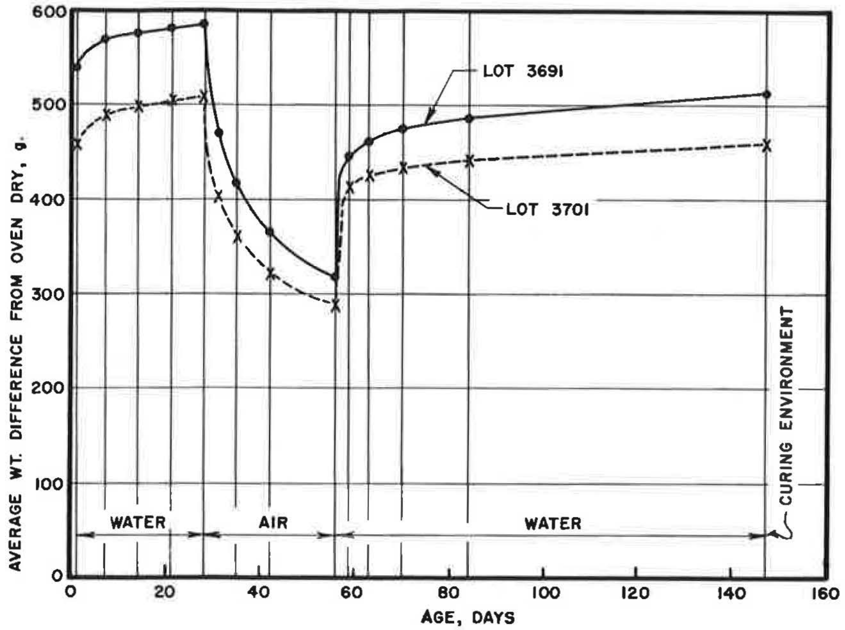

Figure 3. Moisture changes during curing of concretes with chert gravels.

With either aggregate, as already discussed, resistance increased greatly as the specimens were progressively dried for longer periods. The important indication, however, is that this improvement in performance was not forfeited by resaturation even when total saturation exceeded levels at which resistance had been very poor for specimens never previously dried. For example, specimens with lot 3701 chert, resoaked for 14 days after drying, had been restored to within less than 55 g of their 28-day weight but withstood 348 cycles of freezing and thawing. Less saturated companion specimens, which had been dried to a point more than 90 g below their 28-day weight, withstood only 21 cycles. The differences are even more remarkable with lot 3691, for which the resistance of partially dried specimens was poorer. As already pointed out, even after 3 months of resoaking when the concrete had been restored to a high degree of overall saturation, the lot 3701 concrete gave a good account of itself, withstanding 176 cycles of freezing and thawing.

The relationships just discussed are shown in somewhat different form in Figure 5. Here, saturation has been expressed as a percentage of the maximum moisture content (at 28 days), and resistance to freezing and thawing in terms of durability factor as defined in ASTM Designation C 291. The progress of drying and resoaking is indicated by arrowheads on the curves. The considerable displacement of the resoaking portion of the curve toward the higher percentages of saturation demonstrates the lasting benefit of the drying period. At anything above about 65 percent of saturation, the concretes that had not been previously dried performed poorly. On resaturation after drying, the concrete could tolerate 80 percent saturation or more and still give good performance. It appears that, during the initial drying, water tends to remain in the aggregate particles where it causes disruptive expansion, on freezing. Once dried, however, the particles reabsorb water reluctantly. In the resoaked concrete, a greater proportion of the total absorbed water is in the cement paste where it is prevented by the entrained air from causing damage.

In summary, this phase of the investigation illustrates a simple but most important requirement for the assurance of successful performance from the chert gravel concretes. If opportunity is provided for the concrete to lose excess moisture before being frozen, supplemented by reasonable efforts to prevent excessive resaturation disruption from freezing can almost certainly be avoided.

TABLE 4

EFFECTS OF SIZE, SOURCE OF CHERT, CEMENT FACTOR, AND CURING ON CONCRETE DURABILITY

Lot No.	Max. Size (in.)	Cement Factor (sacks)	Sand (%)	b/bo	Batch Ref. No.	Cement (sacks/ cu yd)	Water (gal/ cu yd)	Slump (in.)	Air (grav.) (%)	Unit Weight (pcf)	Freezing-and-Thawing Tests			
											Cycles to 50% E		Dur. Fac., 100 Cyl.	
											Curing A[a]	Curing B[b]	Curing A[a]	Curing B[b]
3691	1	5.0	38.9	0.686	1C5	5.10	31.2	3.0	5.0	137.5	27	251	14	97
					1D5	5.12	31.2	2.6	4.5	138.2	18	420	9	92
					Avg.	5.11	31.2	2.8	4.8	137.8	22	336	11	94
		7.0	35.1	0.682	1C7	7.11	34.7	3.3	4.0	138.6	8	121	4	63
					1D7	7.10	34.9	3.1	3.9	138.6	17	41	8	20
					Avg.	7.10	34.8	3.2	4.0	138.6	12	81	6	42
	½	5.0	54.3	0.500	2C5	4.99	38.8	3.9	5.8	133.9	83	865[c]	42	89
					2D5	5.00	38.5	4.3	5.6	134.3	130	+1,200[c]	55	99
					Avg.	5.00	38.6	4.1	5.7	134.1	106	+1,030[c]	48	94
		7.0	51.4	0.507	2C7	7.09	39.3	3.2	4.9	136.4	77	+1,200[c]	39	94
					2D7	7.09	39.5	4.1	4.7	136.6	42	590[c]	21	101
					Avg.	7.09	39.4	3.6	4.8	136.5	60	+900[c]	30	98
3701	1	5.0	39.4	0.674	3C5	5.01	32.9	2.7	5.4	138.9	58	163	29	70
					3D5	5.03	33.1	4.0	5.1	139.2	76	420	38	87
					Avg.	5.02	33.0	3.4	5.2	139.0	67	292	34	78
		7.0	35.5	0.668	3C7	6.97	35.8	3.6	5.0	139.1	61	178	30	82
					3D7	6.97	36.9	4.3	5.1	139.1	64	174	32	73
					Avg.	6.97	36.4	4.0	5.0	139.1	62	176	31	78
	½	5.0	54.4	0.500	4C5	5.00	38.8	2.8	5.1	136.9	745[c]	1,200[c]	78	89
					4D5	4.99	39.8	3.1	5.2	136.7	625[c]	900[c]	77	91
					Avg.	5.00	39.3	3.0	5.2	136.8	+685[c]	1,050[c]	78	90
		7.0	51.2	0.502	4B7	7.03	40.4	3.6	4.7	137.9	207	940[c]	77	95
					4C7	7.00	40.0	4.2	5.2	137.3	244	530[c]	70	93
					Avg.	7.02	40.2	3.9	5.0	137.6	226	735[c]	74	94

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[a] 7 days in moist room and saturated limewater + 4 days in 70 F air at about 50% relative humidity + 3 days re-immersed in saturated limewater.

[b] 7 days in moist room and saturated limewater + 7 days in 70 F air at about 50% relative humidity.

[c] Extrapolated values; specimens removed after surviving 500 cycles.

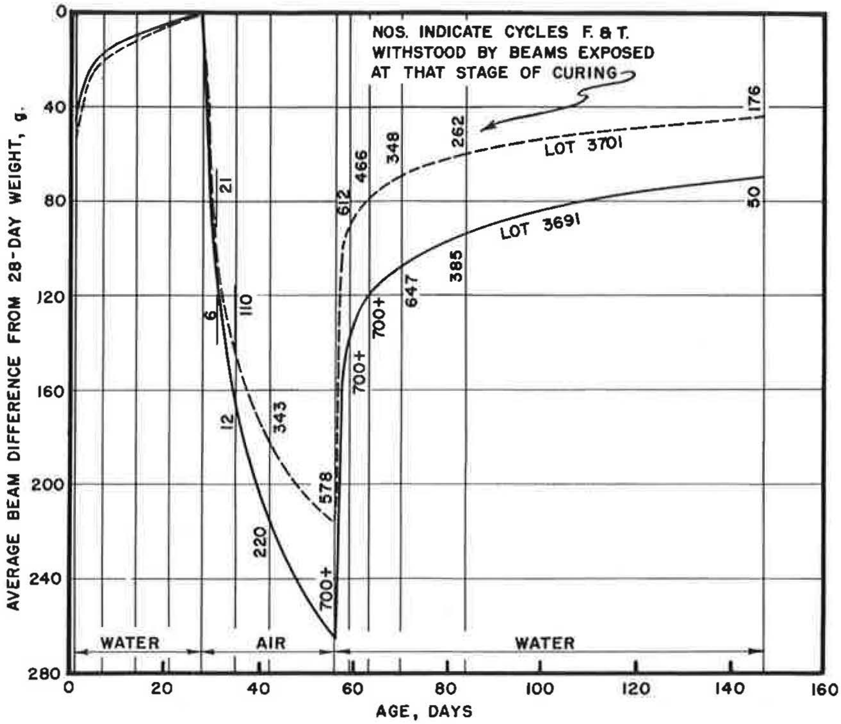

Figure 4. Relation of durability of concrete to moisture content.

EFFECTS OF MAXIMUM AGGREGATE SIZE AND CEMENT FACTOR

Description of Tests

To develop more quantitative information on the improvement in durability caused by using smaller sizes of the chert gravel, comparisons were made between concretes containing the two chert gravels graded to both 1- and ½-in. maximum sizes. For each combination of size and source, cement factors of 5 and 7 sacks per cu yd were employed, making a total of 8 conditions.

Two batches of each kind of concrete were mixed by hand on different days, and beams were molded for freezing-and-thawing exposure after two sequences of curing:

1. To age 7 days immersed in 73 F limewater, followed by 4 days in air at 70 F and approximately 50 percent relative humidity, and 3 days re-immersed in limewater; and
2. To age 7 days in limewater, followed by 7 days in the 70 F air without re-immersion.

These curing conditions, as well as other procedures for preparation of the aggregates, and mixing, molding and testing of concrete, were the same as described for the first group of tests.

Results

Results of the tests are given in Table 4. With one exception, comparability of concrete characteristics among the several conditions was closely maintained. The exception was the 7-sack mixture with the 1-in. maximum size of lot 3691, in which the air content dropped to only about 4 percent compared with 5 percent or slightly higher for the other conditions. This may account for the poor performance of this combination, which is somewhat out of line with the others.

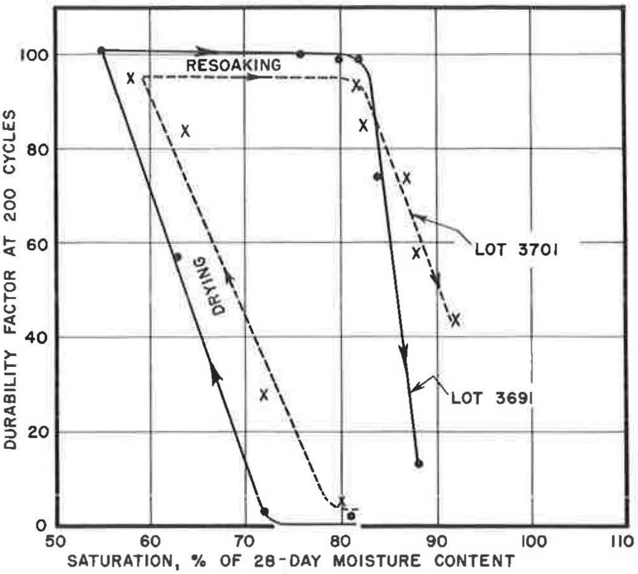

Figure 5. Effects of drying and resaturation on durability of chert gravel concrete.

The data permit several comparisons among the different test conditions. As in other portions of the study, increasing the period of drying before exposure greatly improved the concrete's resistance to freezing and thawing. In fact, except for the low-air-content concrete previously mentioned, all specimens air dried for 7 days before freezing gave a satisfactory to excellent account of themselves.

For otherwise comparable conditions, without exception, concrete with the $\frac{1}{2}$-in. maximum size gravel was much more durable than that with 1-in. maximum. This was true regardless of gravel source, cement factor or curing treatment. In most cases, the number of cycles which the concrete withstood was multiplied several times by lowering the maximum size to $\frac{1}{2}$ in.

The data indicate the 5-sack concretes to have been more durable than the 7-sack, although the difference may not actually be as pronounced as the numbers in the table suggest. There was a slight tendency for the richer mixtures to contain less air but, even though this could account for some of the difference in durability, it appears too small to be a major factor. The data suggest other probable explanations for the seemingly anomalous behavior. First, Table 4 shows that mixing water requirements for the richer concretes were consistently higher than for the leaner mixtures. Although this additional water would tend to be immobilized by reaction with the greater quantity of cement over a long period, it seems probable that, for the relatively short curing used in these tests, there may have been more freezable water in the richer mixes at the time exposure was started.

At least one additional factor probably contributed to the lower durability of the rich mixes. Their lower water-cement ratio would produce a less permeable mortar, tending to retard the loss of freezable water during the interludes of drying. That this actually occurred can be demonstrated from weight measurements made during the curing treatment. For comparable concretes, the net loss of water between 7 days, when the concretes were at their highest saturation, and the beginning of freezing and thawing was always less for the rich than for the lean mixtures. Thus, when exposure to freezing and thawing was started, the richer concretes contained more total water and almost surely more freezable water than the leaner ones. This higher water content coupled with the higher resistance to movement of the water in the richer, less permeable paste, would result in higher disruptive stresses, on freezing.

Comparative performance of the two chert gravels appears reasonably consistent with indications from other portions of the investigation. For specimens resoaked before exposure, the lot 3701 chert produced better resistance than lot 3691. With more thorough drying of the concrete, the performance of both gravels was greatly improved and about equal.

SUMMARY

These investigations provided quantitative information verifying a number of concepts concerning the freezing-and-thawing resistance of concretes made with chert gravel:

1. The relative performance of the chert gravels in relation to other aggregates is likely to be distorted by laboratory tests made on highly saturated concretes containing highly saturated aggregate. The pore structure of the cherts is such that they are highly vulnerable under these conditions. Because concrete in actual practice will almost never be so highly saturated when exposed to freezing, laboratory treatment should logically include a realistic respite from continuous saturation.
2. A moderate amount of drying of the concrete before exposure to freezing and thawing greatly enhances the performance of the chert gravels.
3. Once the concrete has had a reasonable opportunity to dry, its immunity to freezing damage is retained in large measure even after extended resoaking. In these tests, the concrete could tolerate much higher total moisture contents induced by resoaking than were sufficient to cause rapid failure before the concrete had had an opportunity ever to lose the original water.
4. Reducing the maximum size of the chert gravel improves resistance of the concrete to freezing and thawing.
5. Rich concretes will not necessarily be more resistant to freezing and thawing than leaner ones, but relative performance will almost certainly be affected by curing condition and age. The richer cement paste tends to require more mixing water, retard the loss of freezable water due to evaporation, and, by resisting movement of water, increase the stresses developed by freezing. All these factors reduce durability but tend to be offset or overcome by the increased strength of the richer paste or immobilization of the water by chemical combination with the extra cement during long periods of hydration.

Considered in the light of the established service records of many chert gravels, these studies provide encouraging evidence that, for most exposures and with judicious application of normal precautions in removing and excluding water from the concrete, these gravels can be expected to perform well in concrete exposed to freezing and thawing.

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