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Concrete Exposure Tests—Phase 1

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•FIFTEEN test slabs of portland cement concrete were subjected to outdoor exposure and a series of freeze-thaw cycles induced by high concentrations of sodium chloride and calcium chloride.

PURPOSE OF TESTS

The purposes of these tests are (a) to determine the comparative qualities of three wetting agents in producing high compressive strength, low water/cement ratio and workable plasticity; (b) to assay the value of surface sealants presently in use or contemplated for use by the Authority; (c) to obtain comparative data of wet curing vs air curing; and (d) to determine the spall resisting qualities of concrete made with expanded shale as a fine aggregate.

DESCRIPTION OF TEST SLABS

A total of 15 test slabs were cast of a 1:2:3½ concrete (Class A) mix with a water/cement ratio of 5 gal/bag. The slabs are 18 by 18 by 3 in. with a 2- by ¾-in. coping around the top surface to retain water. The slabs were cast in plyscore forms on a sand base. All concrete was mixed indoors at 65 F and cured at the same temperature for 28 days.

To provide uniformity, two master mixes were batched and mixed dry. Batch 1 was a mix using Lone Star Type 2 portland cement, a siliceous sand fine aggregate and limestone coarse aggregate. Batch 2 was a mix using Lone Star Type 2 portland cement, an expanded shale fine aggregate and a limestone coarse aggregate. The gradations of the aggregates are given in Table 1. The master batches were broken down into batches for the individual slabs and the water and admixtures were added. Slump in all cases was 2 in. Table 2 gives the admixtures, air content, slump, method of curing, compressive strength where applicable, and final rating.

TEST PROCEDURE

All blanket curing ceased 14 days after casting; 14 days later the test cylinders were broken by the New York State Department of Public Works Laboratory. The next day the slabs were placed outdoors, the surfaces were flooded with clear water, and the freeze-thaw cycles were begun. Every morning, if a freeze occurred, a mixture of 50 percent NaCl and 50 percent $CaCl_2$ was applied to induce thaw. This cycle was followed for 5 days, after which the slabs were flushed clean and refilled with clear water. The slabs were then left frozen for 48 hr, subject only to temperature-induced thaws. At the end of this period, the deicing salts were again applied for five cycles. During every 5-day period the slabs were either going through freeze-thaw cycles or lay covered with the brine solution. Within the limits of the field testing facilities, the salt solution was maintained at 5 percent.

During the 77 days of the exposure test, the slabs were subjected to 68 freeze-thaw cycles induced by 40 applications of deicing salts and by natural temperature variations. At the conclusion of Phase 1, the first winter's exposure, the slabs were flush-

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Paper sponsored by Committee on Effect of Ice Control.

TABLE 1

AGGREGATE GRADATION

Aggregate	Passing Sieve (%)									
	1½ in.	1 in.	½ in.	¼ in.	No. 4	No. 8	No. 14	No. 28	No. 48	No. 100
Coarse:[a]										
No. 1	-	100	90-100	0-15	-	-	-	-	-	-
No. 2	100	90-100	0-15	-	-	-	-	-	-	-
Comb.[b]	100	93-100	27-58	0-8	-	-	-	-	-	-
Fine:										
Sand	-	-	-	-	100	80.2	45.4	24.6	13.6	8.4
Norlite	-	-	-	-	100	85.6	60.3	37.2	24.1	16.3

[a] Coarse aggregate: Type B limestone; specific gravity, 2.71; Deval abrasion test, 5.7% max. loss by wt; $MgSO_4$ soundness test, 10.0% max. loss by wt at 10 cycles; freeze-thaw test, 3.0% max. loss by wt at 25 cycles.

[b] Not > 50% or < 30% of No. 1 size.

TABLE 2

DESCRIPTION OF TEST SLABS[a]

Slab No.	Fine Aggregate	Cure	Comp. Strength (psi)	Air Content (%)	Rating	Admixture	Sealed
1	S	wet	4,630	7.0	3.50	AB	-
2	S	wet	6,350	7.0	8.50	AC	-
3	S	wet	6,700	4.0	2.50	D	-
4	S	wet	5,590	7.0	7.25	A	-
5	S	wet	6,720	2.0	5.15	-	-
6	S	air	-	8.0	9.45	A	-
7	S	air	-	8.0	9.35	A	O
8	S	wet	-	8.0	9.60	A	O
9	S	wet	-	8.0	8.20	A	H
10	S	air	-	8.0	7.70	A	H
11	S	air	-	2.0	9.80	-	-
12	S	air	-	8.0	5.75	A	P
13	ES	air	-	8.0	10.00	A	-
14	ES	air	-	8.0	10.00	A	P
15	ES	wet	5,150	6.0	9.80	A	-

[a] Symbols used are defined as follows:
A = Darex,
B = Rockwood Wet,
C = Riverside Wetting Agent,
D = Deynor Multi-Wet,
ES = Norlite—expanded shale fine aggregate,
H = Hydrocide-SX-Hycon,
O = 50% boiled linseed oil and 50% mineral spirits,
P = Penetryn D-140 Primer, and
S = sand.

ed clean and left to weather in an exposed position. Phase 2, the second winter, was initiated on Nov. 15, 1963. The ultimate goal is to test the slabs to destruction or to the point where it may be assumed that the surface cannot be destroyed by deicing salts.

EVALUATION CRITERIA

The numerical rating system used for evaluating the tests established a perfect rating of 10 for a durable unblemished surface. A deteriorated test slab received a decreased rating. Five of the total of 10 points were assigned as a measure of the deteriorated area and the remaining 5 as a measure of the deteriorated depth. A 1-in. depth of deterioration by this method would result in no score with regard to the depth factor. Deterioration ½ in. deep would reduce the score of 5 to 2.5. A test specimen having 20 percent of its area affected to a depth of ½ in. would receive a final rating of 6.5 with 4 points for the unaffected area and 2.5 points for the unaffected depth.

The area of deterioration was attained by simple measurements. The depth of deterioration was taken as the average of a group of measurements representative of the points of deepest deterioration. Measurements were taken by bridging the spalled area with a steel straight edge and gaging the depth of penetration with a steel rod ground to a fine point. In the absence of precise measuring instruments, it was obvious that a human element would enter into any rating system devised. Therefore, to assure a correspondence in slab ratings, all rating was done by one individual.

EVALUATION OF TEST SITES

As used here, "spalling" refers to a measurable deterioration in depth; "scaling" refers to the shedding of a lamina of mortar approximately $\frac{1}{32}$ in. thick or less.

Slab 1

This slab shows surface defects on 90 percent of the area. The depth of deterioration extends for $\frac{3}{8}$ in. The addition of the wetting agent produced a loss in compressive strength of 960 psi when compared to the mix control slab. The surface survived 18 freeze-thaw cycles and ten applications of deicing salts before any scaling became apparent. Spalling developed gradually with 90 percent of the surface affected after 42 cycles and 29 applications of salts. During the remaining 26 cycles and 11 applications of chemicals, the depth of the surface pitting increased to $\frac{3}{8}$ in. and the slab showed a weight loss of $1\frac{1}{2}$ lb.

Slab 2

Surface defects appear on 10 percent of the area. The depth of the deterioration extends for $\frac{3}{16}$ in. The use of the wetting agent produced an increase of 760 psi over the compressive strength of the control slab. The surface survived 16 freeze-thaw cycles and nine applications of deicing salts before any surface defects became apparent. After the initial pitting, the slab went through 33 additional freeze-thaw cycles and 23 additional applications of deicing salts before any further deterioration was discernible. At this time the surface deterioration progressed to a light scaling and the remaining 19 freeze-thaw cycles and eight applications of chemicals did not produce a worsening of this condition. The slab showed a weight loss of $\frac{3}{4}$ lb.

Slab 3

This slab shows surface defects on 100 percent of the area. Deterioration extends to $\frac{1}{2}$ in. in depth. The use of the wetting agent produced an increase of 1,100 psi over the compressive strength of the control slab. The surface survived 14 freeze-thaw cycles and eight applications of deicing salts without any apparent damage. From this point the deterioration was exceedingly rapid and an additional 12 freeze-thaw cycles with eight applications of deicing chemical caused the 100 percent destruction of the surface. The slab showed a weight loss of $1\frac{1}{2}$ lb.

Slab 4

This was the control slab for evaluating the relative performance of the wetting agents. Surface defects appear on 30 percent of the area. The depth of the deterioration extends to $\frac{1}{4}$ in. The surface survived 18 freeze-thaw cycles and ten applications of deicing salts before scaling became apparent. The spalling developed gradually requiring an additional 27 cycles and 16 applications of deicing salts. The remaining 23 cycles and 14 applications of chemicals deepened the spalls. No weight loss was shown during exposure.

Slab 5

This slab shows surface defects on 60 percent of the area. The depth of deterioration extends to $\frac{3}{8}$ in.

The composition and casting of this slab vary from control slab 4 only in the absence of an air-entraining agent. The 2 percent air entrainment was induced solely by the cement. The surface survived 14 freeze-thaw cycles and eight applications of deicing salts without any apparent damage. A further 27 cycles and 16 applications of deicing salts produced only light scaling. From this point, deterioration accelerated and an additional five cycles and four applications of chemicals produced heavy spalling over 60 percent of the area. The remaining 22 cycles and 12 applications of chemicals added to the depth of deterioration. There was a weight loss of $\frac{3}{4}$ lb during exposure.

Slab 6

This slab shows surface defects on 5 percent of the area. The depth of the defects is $\frac{1}{16}$ in. This slab varies from control slab 4 in that it contains 1 percent more air and was air cured rather than wet cured. The surface survived 18 freeze-thaw cycles and ten applications of deicing salts without any apparent defects. An additional 26 cycles and 16 applications of chemicals produced only minor scaling on 10 percent of the surface. The remaining 24 cycles and 14 applications of salts produced no worsening of the open area. This slab showed an increase in weight of $1\frac{1}{2}$ lb after exposure.

Slab 7

This slab shows minor surface defects on 10 percent of the area. The depth of the scaling is approximately $\frac{1}{32}$ in. This slab is identical with slab 6, except for the addition of a seal coat of boiled linseed oil and mineral spirit. The sealant was applied 24 hr after casting. The minor marring or stipling of the surface was probably due to this early application of a sealer. The surface survived 44 freeze-thaw cycles and 28 applications of deicing salts before the minor scaling appeared. The remaining 22 cycles and 12 applications of chemicals produced no further deterioration. There was an increase in weight of $\frac{3}{4}$ lb after exposure.

Slab 8

This slab shows minor surface defects on 5 percent of the area. The depth of these defects is approximately $\frac{1}{32}$ in. The sealant was applied after fourteen 14 days of curing. The resistance of the surface to spalling closely paralleled that of slab 7. It required the same number of freeze-thaw cycles and the identical amount of deicing salts to produce minor scaling on both slabs. On this slab, however, the area affected was one-half of that affected on slab 7. The additional cycles and chemicals produced no further deterioration. Weight increased 1 lb after exposure.

Slab 9

Two coats of the sealer were applied after 14 days. This slab shows surface defects on 30 percent of the area. The spalls extend to a depth of $\frac{1}{16}$ in. The surface survived 18 freeze-thaw cycles and ten applications of deicing salts without any apparent defects. The next 26 cycles and 16 applications of chemical produced superficial scaling. With the remaining 24 cycles and 14 applications of salts, the superficial scaling spread to 30 percent of the surface. The slab showed a weight loss of $\frac{1}{2}$ lb during exposure.

Slab 10

Two coats of the sealer were applied after 48 hr. This slab shows minor scaling on 40 percent of the area. The spalls extend to a depth of $\frac{1}{16}$ in. The surface survived 49 freeze-thaw cycles and 31 applications of deicing salts before any surface defects appeared. The remaining 19 cycles and nine applications of chemical spread this superficial scaling, but with no appreciable penetration. The slab showed an increase in weight of $1\frac{1}{4}$ lb after exposure.

Slab 11

The slab was cast from the basic mix without any admixtures or sealants. It shows minor pitting. The combined areas are equal to about 1 percent of the surface. The depth of the pit marks range from $\frac{1}{16}$ to $\frac{1}{4}$ in. The pitting occurred after 18 freeze-thaw cycles and ten applications of deicing salts. An additional 50 cycles and 30 applications of chemicals failed to produce any additional deterioration. The slab showed an increase in weight of $1\frac{1}{2}$ lb after exposure.

Slab 12

Two coats of sealer were applied after 48 hr. This slab shows heavy scaling of 60 percent of the area. The depth of deterioration extends to $\frac{1}{4}$ in. The surface survived

49 freeze-thaw cycles and 31 applications of deicing salts before any defects became apparent. Once spalling started the deterioration was exceedingly rapid, the remaining 19 cycles and nine applications of chemicals doing the final damage. The slab showed a weight loss of ½ lb.

Slab 13

This slab shows no defects after the entire test of 68 freeze-thaw cycles and 40 applications of deicing salts. There was no weight change during exposure.

Slab 14

Two coats of sealer were applied after 48 hr. This slab shows no defects. The only apparent effect of the freeze-thaw cycles and the deicing salts was the peeling of the top coat of the sealer after 56 days of exposure. There was no weight change during exposure.

Slab 15

This slab shows minor pitting. The combined areas of the pits are equal to approximately 1 percent of the surface. The depth of the pits range from $\frac{1}{16}$ to ¼ in. The pitting appeared after 63 freeze-thaw cycles and 36 applications of deicing salts. The extent to which the pitting would have progressed is uncertain because there remained only five more cycles and four additional applications of chemicals to complete the first phase of the test.

TRENDS AND IMPRESSIONS

At the conclusion of Phase 1 of the test, two trends of particular interest were noticeable:

1. Where the slabs were permitted to cure in the open air but shielded from direct sunlight and wind-drying, the average rating after exposure was 8.88. This average is based on ratings of seven of the 15 slabs. Of the eight slabs that were cured with wet burlap, the average rating was 6.81. Five of the seven air-cured slabs had ratings greater than 9.00, whereas only two of the eight wet-cured slabs survived the tests with a rating of 9.00 or better.
2. Slabs made of concrete in which the fine aggregate was expanded shale showed greater resistance to deicing salts and freeze-thaw cycles than slabs in which conventional sand was used. Three slabs were cast of concrete containing expanded shale fine aggregate. Of the three, two were air-cured and one had a wet cure of 14 days. One of the air-cured slabs was sealed with two coats of Penetryn D-140 Primer; the other air-cured slab was untreated. The untreated slab gave a performance equal to the sealed specimen. The wet-cured slab that had not been sealed showed minor pitting and finished with a rating slightly below the two air-cured specimens.

The following impressions, rather than conclusions, have been gathered from Phase 1:

1. The choice of a wetting agent should be carefully weighed and considered. Of the three used in the test, one seemed to serve no useful purpose. In fact, its action was detrimental in that it lowered the compressive strength of the mix 17.1 percent below that of the control slab. The other two, Riverside Co. Wetting Agent and Deynor Multi-Wet, increased the compressive strength by 13.6 percent and 19.6 percent, respectively. However, the specimen with the highest compressive strength proved to be the most susceptible to the ravages of deicing salts. There was no appreciable difference in the workability of the test mixes containing wetting agents when compared to the test mix of the control slab without a wetting agent. No conclusion should be reached from this fact, however, because experience in the field with larger batches has consistently shown that the addition of 4 oz of Deynor Multi-Wet per cubic yard of concrete will allow a 15 percent reduction in water without any reduction in the slump.
2. Of the sealants used on the slabs made with conventional mixes, the mixture of 50 percent boiled linseed oil and 50 percent mineral spirits was the most effective.

The material appears to be slightly more effective when applied 14 days after casting than when it was applied 1 day after casting. This is borne out by a rating of 9.60 on the 14-day old slab, as against a 9.35 rating on the 1-day old slab. The silicone-type sealer was considerably more effective when applied to a 14-day old slab vs 2-day old specimen. The ratings were 8.20 and 7.70, respectively.

3. Of interest is a comparison between slabs 4, 5 and 11. These slabs are basically the same mix with slab 4 having 7 percent air entrainment and 14-day wet cure, slab 5 having 2 percent air entrainment and a 14-day wet cure, and slab 11 having 2 percent air entrainment and air curing. The ratings of these slabs are 7.25, 5.15, and 9.80, respectively. The first two follow the classic pattern that a reduction in air content increases the susceptibility to spalling. Slab 11 with its low air content and anti-spalling character indicates that further testing of curing methods is warranted.

SUMMATION

Phase 1 of the Thruway's concrete exposure tests has been concluded. Phase 2 will be a continuation of the tests on the original 15 slabs and additional slabs necessary to test the trends established in Phase 1. Phase 2 will cover the evaluation of the four bridge sites where concrete repairs were made in the summer of 1963 using expanded shale as a fine aggregate. Results obtained with this material in the exposure test warranted their use in a field installation.

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Field and Laboratory Air-Content Studies of Salt-Damaged Concrete Structures

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A paper dealing with the first phase of "A Survey of Air-Entrained Structures in Illinois" was published in HRB Bulletin 323. Data obtained during the second phase of that survey are presented. To determine the uniformity and effectiveness of air entrainment, and the extent of damage to air-entrained concrete bridges attributable to the action of salt, an investigation of all structures constructed in Illinois with air-entrained concrete was started in 1960.

Of the 879 bridges surveyed, 503 were studied in some detail and 67 were given a thorough investigation, including drilling of cores for air-content studies. The adequacy of the entrained air and preventative measures and treatments are discussed.

•DURING 1960 an investigation was undertaken in Illinois to determine the extent of concrete disintegration on structures that was caused by salt and to determine the air content of the concrete in these structures. The physical survey of these structures included not only the concrete deterioration attributable to the application of chloride salts for ice removal but also all cracks, popouts, and pitting, even though air entrainment might have no direct bearing on these. The use of air entrainment became mandatory in Illinois in 1947. Inasmuch as this survey was primarily to learn how effective air entrainment has been, the structures studied were those built between 1947 to 1959.

This study of surface disintegration on structures due to salt had three main objectives: (a) to ascertain whether air entrainment does not impart adequate resistance to scaling, (b) to determine whether concrete placed in structures always contains adequate entrained air, and (c) to determine the need for other preventive measures or treatments.

The field survey of the structures included all types of distress. The scope of this paper, however, is limited to an analysis of the apparent damage resulting from salt applications and how this is influenced by the air content of the concrete.

FIELD OBSERVATIONS

Original Survey

During the fall, winter, and early spring of 1960 and 1961 a complete physical survey was made on 879 concrete structures. The data included ratings as to the degree of scaling, aggregate popouts, surface pitting, hairline cracks, larger cracks and leaching. The study was done separately for deck, gutter, hubguard, and sidewalk. Also included were certain construction information and sources of materials.

Of the 879 bridges reported, 376 had undergone since original construction some sort of modification, including widening and the addition of a bituminous surface. These structures are referred to as modified bridges, whereas the remaining 503 structures are designated as original bridges. Only this latter group is considered herein.

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As an example of the degree of scaling in the deck, 5 percent had light scaling, 3 percent had medium scaling, 4 percent had heavy scaling, and 1 percent was classified as threatening structural failure. The degree of scaling in the gutter, hubguard, and sidewalk was similar to that in the deck.

Second Survey

During the early part of 1962 a second survey of 67 of the original structures was made by a team of engineers from the Illinois Bureaus of Construction, Design, Maintenance, Materials, and Research and Planning. The structures selected were distributed throughout the State with approximately seven structures to each of the ten highway districts.

On each of these structures, locations were pinpointed for the drilling of 2-in. diam cores for air-content determinations. The cores, approximately 4 in. long, were drilled from scaled and unscaled areas of the deck, gutter area, and sidewalk.

LABORATORY TESTS

Method of Air Determination

A high-pressure air meter was used to determine the air content of the cores. This meter operates on the same principle as that used for determining the air content of concrete in the plastic state. The major difference is that 15 psi pressure is used for the test of concrete in the plastic state, whereas 5,000 psi pressure is utilized when determining the air content of hardened concrete. The accuracy of this meter has been verified several times since it was built in 1953.

Pavement Cores

The high-pressure meter has been used in approximately one-third of the 8,094 routine air tests made on 4-in. diam pavement cores between 1954 and 1961. The average air content of these cores is 3.7 percent, whereas 62,107 air tests in the field on the plastic concrete from the same jobs gave an average air content of 4.3 percent. Most of the 0.6 percent differential is probably due to loss of air during surface vibration of the concrete. Various field tests have shown approximately 0.5 percent loss by tests of the plastic concrete before and after such surface vibration.

Structure Cores

From the 67 structures, 604 2-in. diam cores were drilled and tested in a high-pressure meter of the same design as, but smaller than, that used for the 4-in. pavement cores. A summary of these data is given in Table 1.

TABLE 1

AVERAGE RESULTS[a] OF AIR CONTENT DETERMINATIONS

District	Average Air Content of Cores (%)							
	Deck		Gutter		Sidewalk		Over-All Average	
	Scaled	Unscaled	Scaled	Unscaled	Scaled	Unscaled	Scaled	Unscaled
1	1.7(20)	3.5(33)	1.5(5)	4.2(11)	2.2(5)	3.5(13)	1.8(30)	3.6(57)
2	1.7(11)	1.6(20)	1.0(12)	3.2(11)	0.1(10)	0.8(14)	1.0(33)	1.7(45)
3	1.4(5)	2.1(25)	1.1(15)	1.8(5)	0.6(8)	1.7(11)	1.0(28)	2.0(41)
4	3.9(14)	3.8(26)	2.2(2)	3.3(3)	1.0(6)	2.8(11)	2.9(22)	3.5(40)
5	0.4(4)	2.9(18)	-	2.2(1)	1.4(7)	2.6(2)	1.0(11)	2.8(21)
6	1.1(7)	2.0(11)	0.0(3)	1.5(2)	1.3(6)	1.5(7)	1.0(16)	1.7(20)
7	2.4(6)	2.8(15)	1.7(2)	2.1(4)	2.7(5)	2.9(17)	2.4(13)	2.8(36)
8	1.9(8)	2.8(24)	4.8(6)	2.3(4)	3.2(11)	3.2(16)	3.2(25)	2.9(44)
9	2.6(7)	2.7(24)	2.0(9)	3.4(4)	2.4(4)	-	2.3(20)	2.8(28)
10	1.7(27)	2.1(28)	0.2(2)	1.9(8)	1.2(4)	1.5(5)	1.5(33)	2.0(41)
Avg.	2.0(109)	2.7(224)	1.6(56)	2.9(53)	1.6(66)	2.3(96)	1.8(231)	2.6(373)

[a] Figures in parentheses are number of cores tested.

To verify test procedures, laboratory control specimens were tested with the field cores. Five batches each of crushed stone concrete and gravel concrete were mixed and 6- by 6- by 30-in. test beams were cast. The air contents were varied from 0.2 to 6.5 percent. Two-inch and 4-in. cores were drilled from the beams and air contents were determined by the high-pressure meter. The average of ten determinations on the concrete in plastic state was 2.8 percent. Seventy-eight tests on 2-in. cores gave an average air content of 2.6 percent and 40 tests on 4-in. cores gave an average air content of 2.8 percent. Inasmuch as these tests were intermingled with the 604 tests made on the structure cores, it is believed that the results of the air tests on the structure cores are fairly accurate. There is a slight indication that the 2-in. cores may give results a couple of tenths or so less than the 4-in. cores. The results of these tests are given in Table 2.

The over-all average air contents of 1.8 and 2.6 percent (Table 1) for the scaled and unscaled areas of the structures are entirely too low to provide the adequate protection against salt damage expected of air-entrained concrete. The large proportion of cores with low air contents indicates inadequate control of truck loads of concrete. There is no doubt that a considerable number of truck loads of non-air-entrained concrete were placed in these structures. Also, a considerable loss of entrained air may have taken place at certain locations due to excessive internal vibration.

One disconcerting part of the data was that some cores that were drilled from scaled areas showed adequate air entrainment. This condition is quite different that that found in pavement concrete where practically no scaling is found on pavements containing adequate entrained air. Due to various conditions it is impossible to establish an exact percentage of entrained air below which protection will always be inadequate and above which protection will always be sufficient. The percentage may be somewhere between 2.5 and 3.0. For adequate protection, however, the percentage of remaining entrained air should be greater than 4 percent.

Sprinkling of Concrete Surface

One factor that might make spots of scaling on air-entrained concrete more prevalent on structures is the greater use of water sprinkled on the surface of the concrete to facilitate finishing operations. To study the effect that this practice has on the surface of the concrete, an investigation of the problem was made on slabs cast outside the laboratory. A truck load of ready-mixed concrete that was going to a structure was diverted past the laboratory so that four 24- by 48- by 4-in. slabs could be cast. The concrete was given internal vibration and was struck off by a vibrating screed. The slabs were finished similar to a bridge deck, except that one slab had no water sprinkled on it, whereas the other three had various amounts sprinkled on them with a calcimine brush. This sprinkling took place after the initial strike off and before the final surface finishing. If the water penetrates the concrete to a depth of ⅛-in., which is a reasonable assumption, the surface concrete would have the water-cement ratio increased 1¼ gal/bag of cement by one light swish of the brush. The three slabs were treated so that each unit area had the equivalent of one light stroke of the brush, three light strokes of the brush, and two heavier strokes, respectively. Therefore, the first treated slab had 1¼ gal of water added, the second had 3¾, and the third about 5 gal/bag of cement. There is no doubt but that some of this water evaporated.

TABLE 2

RESULTS OF AIR CONTENT DETERMINATIONS ON LABORATORY CONCRETE IN PLASTIC AND HARDENED STATE

Core Size (in.)	Average Air Content (%)			
	Gravel Aggregate		Crushed Stone Aggregate	
	Hardened Concrete	Plastic Concrete	Hardened Concrete	Plastic Concrete
2 × 6	0.2	0.2	0.4	0.4
4 × 6	0.2		0.6	
2 × 6	1.4	1.4	1.8	1.3
4 × 6	1.4		1.4	
2 × 6	1.8	2.3	2.8	2.7
4 × 6	1.8		2.8	
2 × 6	3.0	3.6	4.4	4.4
4 × 6	3.3		4.6	
2 × 6	4.2	5.0	6.4	6.5
4 × 6	5.2		6.9	

After curing for 14 days, surface tension tests were made to determine strengths. This was accomplished by gluing 2-in. diam pipe caps to the surface of the concrete with an epoxy and then pulling the caps from the surface. The load, determined by a dynamometer, was converted to pounds per square inch tension to indicate the strength of the concrete surface. There were 14 or more tension tests made on each of the four slabs. The control surface, where no water was sprinkled, gave a strength of 280 psi. The surface of the second slab, where water was sprinkled with one light stroke of the brush, also gave the same 280 psi strength. The third slab, where water was sprinkled with three light strokes of the brush, gave a strength of 210 psi. The fourth slab, which had the water sprinkled on with two heavy strokes of the brush, gave a strength of 200 psi. The slabs were turned over and about six tension tests were made on each of the four slabs. All gave a tensile strength of 285 psi or about the same as the top unsprinkled surface. The tension test apparatus is shown in Figure 1. A curve of the resulting strengths is shown in Figure 2. The loss in surface strength between the unsprinkled concrete surface and the two heavier sprinkled surfaces was about 25 percent. This weaker surface no doubt was more porous, although there is no test to prove it. It was noted that when water was placed on the nonsprinkled surface and the heavier sprinkled surface, there was visually much more rapid absorption in the latter slab. It would, therefore, be more susceptible to the absorption of salt brines. Perhaps some of the entrained air in the surface of the concrete may have floated out or was worked out of the surface during finishing. All of these conditions lead to less durable air-entrained concrete which would be less resistant to scaling due to salt brines.

PREVENTIVE AND PRECAUTIONARY MEASURES

Number of Tests on Plastic Concrete

At about the same time that the field study was decided on, further steps were taken

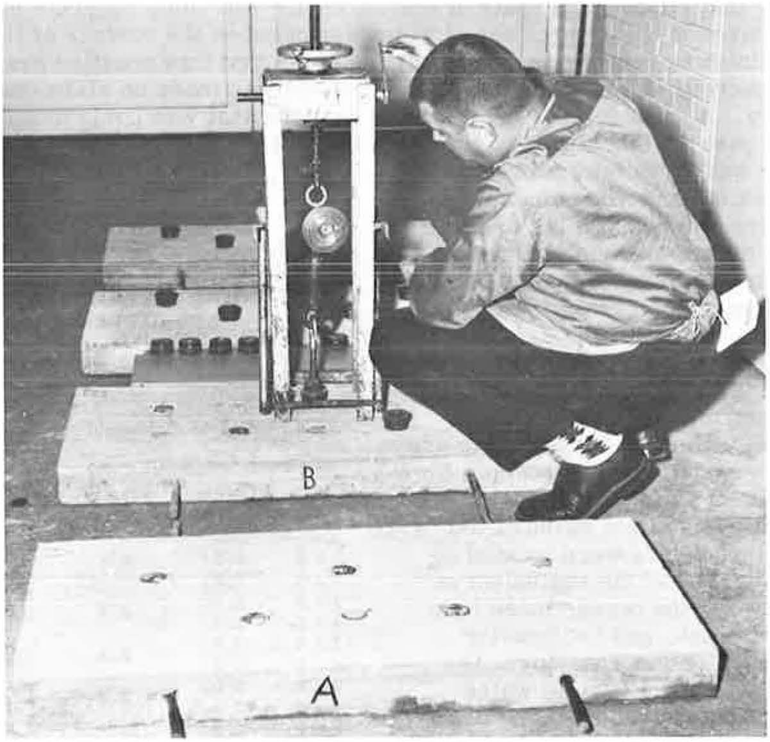

Figure 1. Surface tension test.

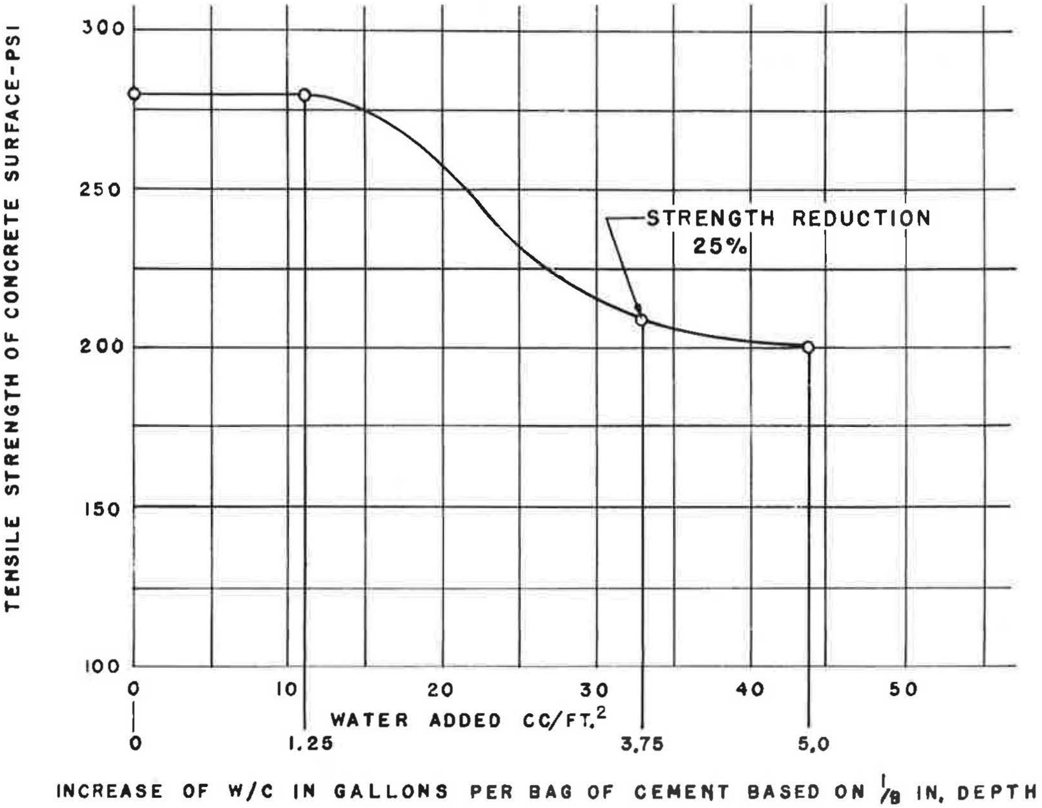

Figure 2. Tensile strength of concrete surface vs quantity of water sprinkled during finishing.

in the field control of the plastic concrete to insure initially that all concrete had the proper amount of entrained air when it was placed in the structure. In 1960 it was required that an air test be conducted on each load of ready-mixed concrete delivered for placement in decks, hubguards, sidewalks, handrails, and other parts of the structures that would be exposed to salt or splashes of brine. To check the effectiveness of this requirement, 32 cores were drilled for air content tests from three structures built during 1962. Results of these tests, shown in Table 3, indicate a 0.8 percent loss of air or slightly more than was shown for pavement concrete.

Amount of Entrained Air

The second measure taken to provide greater protection to the concrete was to raise the specifications of air content limits of 3 to 5 percent to 4 to 6 percent in 1961. At the present time the specifications are being changed to 4 to 7 percent. These changes are for pavement concrete, as well as for structure concrete. The increased air content seems entirely warranted, especially in highway structure concrete.

Linseed Oil Treatment

The third measure taken may be considered as temporary assistance to the air-entrained concrete. On July 1, 1962, the treatment of all new structure decks with a mixture of 50 percent boiled linseed oil and 50 percent mineral spirits was made effective. Whereas it is known that concrete with adequate entrained air is very resistant to salt damage, it is also known that if air-entrained concrete has not aged some-

TABLE 3

RESULTS OF FIELD STUDIES ON AIR CONTENT OF HARDENED AND PLASTIC CONCRETE

Tests	Air Content (%)		
	Bridge A	Bridge B	Bridge C
Hardened concrete[a]	5.8	6.3	9.2
	5.5	5.7	8.4
	5.4	4.8	8.1
	5.2	4.4	7.6
	4.9	4.1	7.5
	4.8	3.9	6.1
	4.1	3.8	5.4
	3.5	2.4	5.0
	3.4	2.2	3.2
	3.4	1.8	3.0
	2.6	-	2.1
Average	4.4	3.9	6.0
Plastic concrete[b]			
High	7.1	6.4	8.4
Low	4.0	3.4	5.5
Average	5.6	4.7	6.5

[a] Using 2-in. cores.

[b] Number of loads of concrete tested for Bridges A, B, and C were 45, 30, and 15, respectively.

what and dried out, it has not developed this high resistance to salt action. Laboratory tests have shown that linseed oil treatment will not prevent salt damage, but it is hoped that the treatment will act as a retardant during the early age of the concrete and until the air-entrained concrete has developed its full potential for resistance to salt action.

CONCLUSIONS

From the data presented, the following conclusions can be made:

1. From 6 to 13 percent of the original air-entrained bridges showed scaling in varying degrees in the deck, gutter, hubguard and sidewalk.
2. Between 1947 and 1959, the control and number of air tests made were inadequate to assure that the proper amount of entrained air was always incorportated in the concrete.
3. On the average, the 1.8 percent entrained air obtained from the cores drilled from scaled areas is too low for adequate protection.
4. The average air content of 2.6 percent for the cores drilled from unscaled areas is too low for assurance that scaling will not develop.
5. A loss of 0.5 to 1.0 percent of entrained air may be expected in the concrete between the plastic and hardened state, probably 0.5 percent for pavement concrete and about 1.0 percent for structural concrete.
6. The need for more rigid control of air content by increase in the required number of air tests and increase in the specified air content is borne out by the data.
7. Sprinkling of air-entrained concrete surface may cause a reduction of 25 percent in surface strength and will result in a surface more permeable to salt brines.

Development of a Concrete Admixture to Improve Freeze-Thaw Durability

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A study to determine the effect of various silicone admixtures on the resistance of concrete to freeze-thaw conditions has resulted in the development of a new silicone admixture (Dow Corning 777).

The most important improvement with the use of this admixture is the increase in resistance of concrete to the action of freezing and thawing in the presence of deicing chemicals. Using the Conrad rapid-cycle freeze-thaw test apparatus, specimens were continuously exposed in the presence of a 10 percent sodium chloride solution. The concrete specimens containing the admixture showed more than 50 percent improvement in durability compared with air-entrained control specimens. Scaling slab specimens continuously exposed to 2 percent sodium chloride and undergoing one freeze-thaw cycle per day also show good improvement in scaling resistance. Other improvements include increases in compressive strength, flexural strength, and bond to reinforcing steel. Although the admixture produces extended set times in concrete, field trials have indicated that successful placement is easily accomplished using standard techniques.

•SEVERAL YEARS ago it was discovered that the addition of certain silicon compounds to concrete would contribute to the freeze-thaw durability. This led to a study of the freeze-thaw properties of concrete and of methods of determining if any one of a wide variety of silicone chemicals could be used to improve concrete durability under very severe freeze-thaw conditions in the presence of ice-melting salts. Many silicones and silicon chemicals were tested as additives and one organo-siloxane material appeared most beneficial.

This new material is a unique compound from the family of chemical substances broadly identified as silicones. It bears no direct relationship, however, to the earlier types of silicones used as surface-applied water repellants or those materials initially tried as admixtures, many of which have been previously reported. For purposes of identification, this new admixture will be referred to here as "the silicone admixture." Besides improving freeze-thaw resistance, this new product provides substantial increases in compressive and flexural strengths and improves bond to reinforcing steel.

CONCRETE MATERIALS AND DESIGN

A considerable amount of study and care was devoted to selecting, preparing and proportioning all components used in the test program to eliminate as far as possible the usual variables due to non-uniformity of materials. Freeze-thaw durability, as well as other important physical properties, depends greatly on the care exercised in preparing the concrete.

Aggregates

Because of their high chemical purity traprock from New York State and Long Island silica sand were chosen as aggregates for this program. Both the coarse and fine aggre-

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TABLE 1

PROPORTIONS BY SIZE OF AGGREGATES USED

Aggregate	Proportion (% by wt)										
	1½-1 In.	1-¾ In.	¾-½ In.	½-⅜ In.	⅜ In.-No. 4	Nos. 4-8	Nos. 8-16	Nos. 16-30	Nos. 30-50	Nos. 50-100	Nos. 100-200
N. Y. traprock	5	20	30	15	25	5	—	—	—	—	—
L. I. sand	—	—	—	—	2	15	20	20	20	15	8

TABLE 2

CHEMICAL ANALYSIS OF AGGREGATES

Components	Percent	
	N. Y. Traprock	L. I. Sand
SiO_2	53.73	95.98
Al_2O_3	13.13	1.34
FeO	10.14	—
Fe_2O_3	2.65	0.55
CaO	9.09	0.19
MgO	4.78	0.28
Na_2O	3.25	0.20
K_2O	1.12	0.15
SO_3	0.01	—
CO_2	0.33	—
S	0.027	—
TiO_2	—	0.27
ZnO_2	—	0.34
Cr_2O_3	—	0.03
MnO_2	—	0.18
Organic C	0.01	—
Total C	0.10	—
Loss on ignition	0.53	0.24

TABLE 3

ANALYSIS OF BRAND E CEMENT[a]

Components	%
SiO_2	22.04
Fe_2O_3	2.36
Al_2O_3	4.62
CaO	62.94
MgO	2.72
SO_3	2.33
Ignition loss	1.80
Total	98.81
Free CaO	0.54
Alkalies as:	
Na_2O	0.30
K_2O	0.65
Total as Na_2O	0.73
Corrected calulated compound composition:	
C_3S	45.4
C_2S	29.0
C_3A	8.3
C_4AF	7.2
$CaSO_4$	4.0

[a] Blaine fineness, 3,290 sq cm/gm.

gates were dried, screened to size, and then remixed in predetermined proportions for each batch (Table 1). This procedure assured an accurate and uniform gradation between batches throughout the test program. Chemical analyses of the aggregates are given in Table 2.

Cement

Different brands of cement exhibit considerable variation in freeze-thaw durability and other physical properties. For this reason, the cement used in the program was purchased in quantities of 20 to 40 bbl to eliminate this variable throughout a given test series. The cement was stored in air-tight steel drums and used within a 6-mo period. Most of the results presented were obtained using cement Brand E. A chemical analysis of this cement is presented in Table 3.

Mix Design

Concrete designs were calculated using the recommended procedure outlined by the American Concrete Institute (ACI 613-54). A 6.32 sk/cu yd mix was used in most basic testing. Quantities used to produce 1 yd of concrete with this design are 593 lb cement, 1,880 lb coarse aggregate (traprock), 1,305 lb fine aggregate (silica sand), and 290 lb water (w/c = 0.49). The aggregate weights are on a dry basis.

PREPARATION OF TEST SPECIMENS

Mixing

Each batch of concrete was made by placing the stone, sand, and cement in a rotating inclined drum-type mixer with a rated capacity of 1¼ cu ft. The mortar content of the batch design was increased by 4 percent. This amount of mortar was found to adhere to the sides of the mixer after placing, allowing a more rapid preparation of concrete containing different admixtures because it was not necessary to "butter" the mixer before each pour. Sand, stone, and cement were dry blended for 2 min. Then admixture and water were added in amounts sufficient to give a 2- to 3-in. slump. A final wet mix of 5 min was given, with any required adjustment of water being made during the first 2 min. After mixing, the concrete was placed in a wheelbarrow and slowly agitated with a mortar hoe while slump and air (ASTM C-231) measurements were taken. Test specimens were then fabricated.

Freeze-Thaw Samples

Rapid-cycle freeze-thaw test specimens were prepared in 3- by 4- by 16-in. molds following procedures outlined in ASTM C-192. The test bars were cured in the mold for 3 days at 100 percent RH and 70 to 75 F. They were then removed from the molds and cured for an additional 11 days under the same conditions. Before freeze-thaw testing, the bars were removed from the humidity room and soaked for 16 hr in the solution in which they were to be tested.

Slow-cycle specimens were also formed according to ASTM C-192; however, the mold was somewhat smaller (7 by 4 by 2¼ in.). The slabs were cured for 7 days at 100 percent RH and then an additional 7 days at laboratory conditions. During the latter period, an aluminum weir was fastened around the perimeter of the specimen so that a ½-in. depth of solution could be retained on the screeded surface. The weir was fastened with room-temperature vulcanizing silicone rubber.

TESTING PROCEDURES

Rapid-Cycle Method

The most frequently used rapid-cycle freeze-thaw tests are freeze in air—thaw in water and freeze in water—thaw in water. Because deterioration of concrete is often associated with deicing salts, tests in salt solutions should also be considered. Samples of liquid, therefore, were taken from the wet surfaces of bridge decks and roadways to obtain some measure of the actual salt exposure. These samples were analyzed for NaCl content and the results are shown in Table 4. The continued evaporation of water from any given area can cause a variation in salt content from very dilute to very concentrated, depending on when the sample was taken. In view of the salt content revealed by these tests, it was decided to evaluate durability by the following rapid-cycle test methods:

1. Freeze in air and thaw in water (ASTM C-291),
2. Freeze and thaw in water (ASTM C-290),
3. Freeze and thaw in 2 percent NaCl solution, and
4. Freeze and thaw in 10 percent NaCl solution.

Freeze and thaw testing in water caused the containers used in the test machines to burst along the seams. Severe deformation of the cans occurred within the first 30 cycles. Because water expands approximately 10 percent during freezing, extreme pressures were being exerted on the test specimens as well as the containers. In all cases, pressure developed in the cans caused the specimens to fracture prematurely within a few cycles. Because all specimens failed before any surface deterioration took place, this test could not be used to measure freeze-thaw durability when run in rigid containers.

TABLE 4

SALT CONTENT OF LIQUID SAMPLES FROM BRIDGE AND ROADWAY SURFACES

Sample Source	NaCl[a]
Heavily traveled city bridge	9.1
	8.6
Expressway bridge	1.6
	0.9
	2.9
	2.4
Expressway catwalk	2.0
Expressway exit	1.5
Expressway roadway	2.7
Expressway entrance	3.2
	1.1
Expressway shoulder	2.5
Municipal street	1.6
Suburban intersection	0.1

[a] Analysis by chloride content; all trace chlorides are computed as NaCl. Analysis for calcium ion showed only trace amounts.

Experimentation with various containers revealed that the problem of testing in water could be solved by removing from the can a portion of one vertical corner and replacing it with a corner made of Silastic silicone rubber, which remains elastic at sub-zero temperatures. With this modification, compressive forces on the test specimen were eliminated and deterioration could be studied without premature cracking. Freeze-thaw testing in 10 percent salt solutions did not require the use of a diaphragm container.

Slow-Cycle Scaling Slab Test

This method was used to study scaling properties of the finished surface only. A 2 percent NaCl solution was placed on the surface and the slab was frozen overnight (16 hr) at -17 F in a vertical household freezer. During the day (8 hr) the freezer was turned off, the doors opened, and the specimens allowed to thaw at room temperature. The 2 percent salt solution was used in most scaling slab tests to secure a rapid rate of deterioration (1). The salt solution was left in continuous contact with the surface and replenished as needed. Once each week the specimens were rinsed with water, examined, and the degree of deterioration recorded against a 10 point reference scale (2). Fresh solution was placed on the surface after each reading (every 5 cycles).

Rapid-Cycle Scaling Slab Test

A rapid-cycle scaling slab test was developed because of the need for studying surface deterioration under something other than 2 percent salt solution. A portion of a Conrad rapid-cycle freeze-thaw machine was modified to accept scaling slab specimens. Test slabs were the same as those previously used in the slow-cycle test. They were sealed in polyethylene bags with water, 2 or 10 percent salt solutions on the surface and allowed to cycle between 0 and 40 F. Once each week (every 41 cycles) the slabs were examined, flushed with water, and rated for scaling condition.

Other Tests

Several other concrete properties were examined using ASTM recommended procedures as follows:

1. Procter set time (ASTM C-403),
2. Shrinkage on 1- by 1- by 10-in. mortar bars (ASTM C-226),
3. Compressive strength on 4- by 8-in. cylinders (ASTM C-39),
4. Flexural strength (ASTM C-293), and
5. Bond to reinforcing steel with failure taken at maximum load (ASTM C-234).

The rate of slump decrease was also measured. Slump measurements were taken in the laboratory at regular intervals until they reached zero. Before each slump test was made, the concrete was remixed for 15 sec to insure homogeneity.

DISCUSSION OF TEST RESULTS

Concrete with the silicone admixture was compared with air-entrained concrete by the four methods previously described under testing procedures.

The results in Table 5 show that the silicone-admixed concrete is superior to air-

TABLE 5

DURABILITY OF CONCRETE SUBJECTED TO RAPID FREEZE-THAW TESTS[a]

Type of Concrete	Air Content (%)	Number of Cycles Until Failure[b]			
		Method 1	Method 2	Method 3	Method 4
Non-air-entrained	1.5	50S	27S	16S	29S
Air-entrained	4.9	> 1,500	225W	150W	250W
	7.6	—	260W	140W	310W
0.3% silicone admixture	5.5	> 1,500	610W	230W	413W

[a] Based on average of three specimens; diaphragm containers used except in Method 1 which does not used containers.

[b] S = failure in sonic modulus (i.e., drop to 60% of the original value); W = denotes failure by 5 percent weight loss (5 percent adopted because surface deterioration was such as to be considered general surface failure).

entrained concrete when tested in water or salt solutions. It also is unaffected by the freeze in air—thaw in water test, further indicating excellent durability.

From this test work, freezing and thawing in 10 percent salt solution was selected as the basic test procedure because it embodied more clearly certain criteria believed necessary to indicate improved durability. This method differentiates between different air levels and produces the general type of surface failure seen in the field. It also incorporates the use of salt known to be present on highway concrete throughout the seasons when freezing and thawing occur.

Rapid Freeze-Thaw Tests With Traprock

During the development of the silicone admixture, several hundred specimens were tested by the rapid freeze-thaw method in 10 percent salt solutions and compared with air-entrained concrete. These tests have shown that both 5 percent air-entrained and admixed concretes fail by a progressive erosion of the exposed surface. Failure (5 percent weight loss) occurred much more slowly, however, when the silicone was used as an integral admixture. In freeze-thaw testing, exact duplication of results from batch to batch could not be obtained. Even with a careful reblending of seven sizes of silica sand and six sizes of traprock for each batch, there was still a considerable scattering of data. Due to this, it was felt that a probability curve would be the most realistic means of presenting a large number of freeze-thaw results.

Figure 1 shows the probability curve developed for both air-entrained and admixed concretes. The mean values of the two curves (probability = 0.5) show air-entrained and admixed concretes have average durabilities of 250 and 560 cycles, respectively. This indicates that about a 120 percent increase in freeze-thaw durability can be expected when the silicone is used as an admixture. A regression analysis of the data used to obtain the probability curve showed that the resistance of the admixed concrete to freeze-thaw deterioration in 10 percent NaCl solution is primarily a function of silicone concentration and not air content.

Effect of Silicone Admixture on Freeze-Thaw Durability of Various Brands of Cement

Because the supply of cement purchased at one time lasted only 6 mo, it was necessary to change cements occasionally. In changing from lot to lot, it was noticed that all cements, even when of the same brand, did not have the same freeze-thaw durability. Figure 2 shows results obtained with several different brands of cement.

Although all cements did not have the same freeze-thaw durability, the improvement produced by the admixture was of the same order of magnitude in each case. These

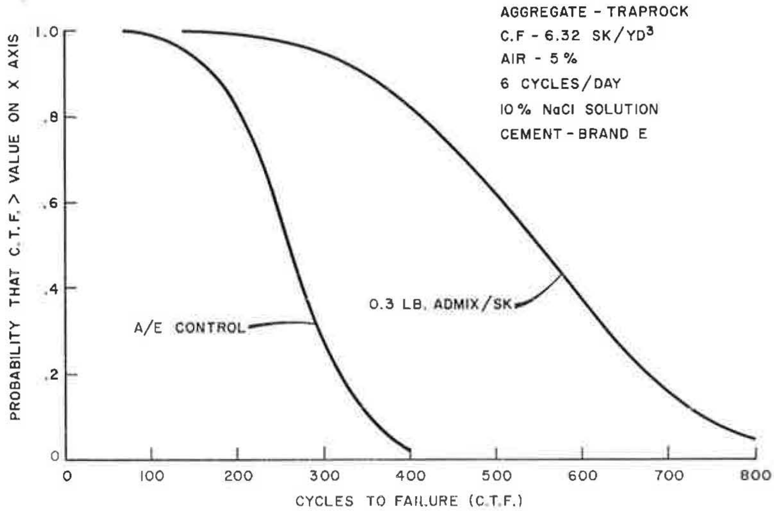

Figure 1. Probability vs cycles to failure.

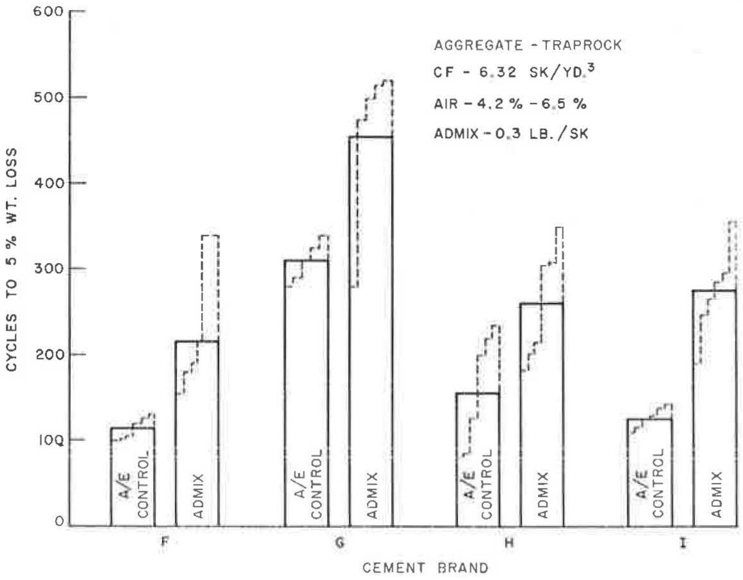

Figure 2. Cycles to 5 percent weight loss vs cement brand.

data indicate that the improved resistance to freeze-thaw in 10 percent salt solution is not peculiar to a given brand of cement.

Effect of Silicone Admixture on Durability of Concrete With Different Cement Factors

Using traprock and silica sand, concrete batches were designed with cement factors of 4, 5½, and 7 sk/cu yd. Figure 3 shows the results obtained with concrete having these cement factors and freeze-thaw tested in 10 percent salt solution. It should be noted that in every case the freeze-thaw durability is increased when the silicone admixture is used.

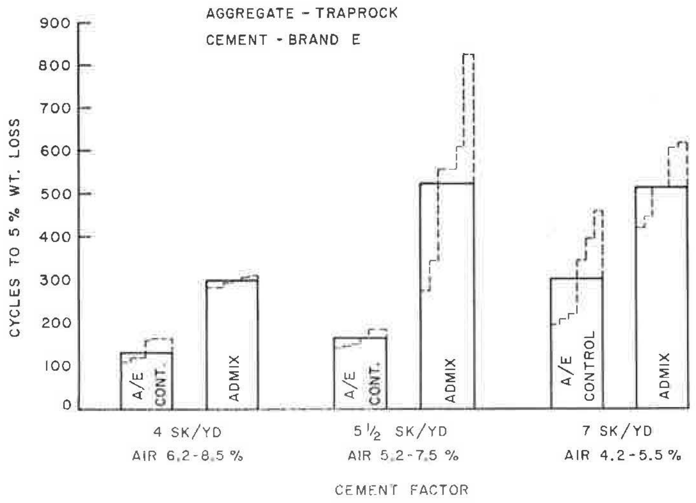

Figure 3. Cycles to 5 percent weight loss vs cement factor.

The addition of 0.3 percent of the silicone admixture improved the durability of a 4-sk design to the point where it is equal to that of a 7-sk air-entrained concrete. However, the reduction of cement content when the admixture is used is not recommended. A large reduction in cement factor would not permit the manufacture of higher quality concrete and this would defeat the purpose of using the silicone admixture. For instance, other properties of concrete, such as abrasion, are of significant importance, and these must also be considered in the selection of the cement factor. These data indicate the admixture can be used in concretes of both high and low cement factor to produce a building material that may be more durable and may require less maintenance than a conventional concrete.

Slow Freeze-Thaw Scaling Slab Tests

Surface scaling observations made on the rapid freeze-thaw test bars indicated that the silicone admixture greatly improved the scaling resistance of the screeded surface. To further evaluate this property, scaling slab tests were run with a 2 percent salt solution as corollaries to the rapid freeze-thaw test.

Figure 4 shows curves of surface scaling rating vs freeze-thaw cycles for air-entrained and admixed concrete. The most rapid rate of deterioration occurs during the first 20 cycles; after this the rate of deterioration is much slower. Concrete containing the admixture shows much improved resistance to scaling in the presence of deicing salts. The admixed specimens at 85 cycles showed less scaling than the air-entrained specimens at 10 cycles. This indicates that about 700 to 800 percent increase in scaling resistance might be expected when the silicone admixture is used.

Scaling slabs were also fabricated from concrete containing different cements. Results of freeze-thaw testing of these slabs are shown in Figures 5 to 8. These curves on the four different cements show the same trend noticed in the Conrad rapid freeze-thaw equipment. Not all cements have the same degree of scale resistance when subjected to slow freeze-thaw under a 2 percent NaCl solution, but the use of the silicone admixture has produced relatively scale-free concrete with all brands of Type I cement used.

Rapid Freeze-Thaw Scaling Slab Test

By modifying a portion of one Conrad machine, rapid-cycle scaling slab tests were run with 2 and 10 percent salt solutions on the surfaces. Figures 9 and 10 depict the

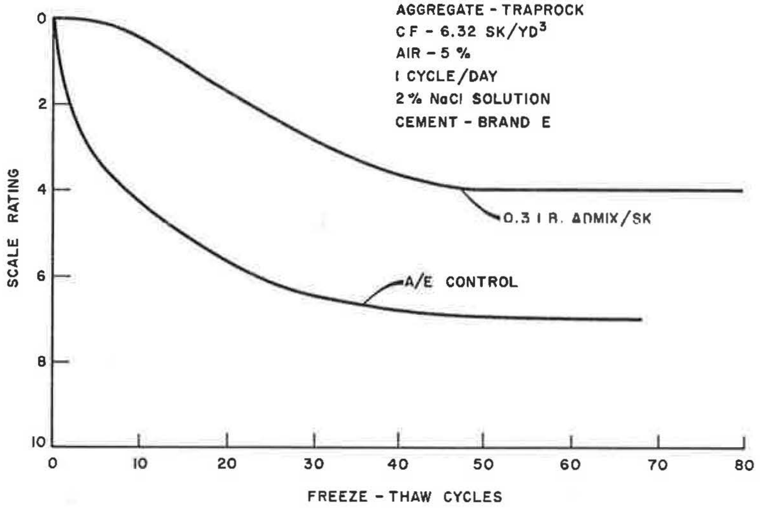

Figure 4. Scale rating vs freeze-thaw cycles.

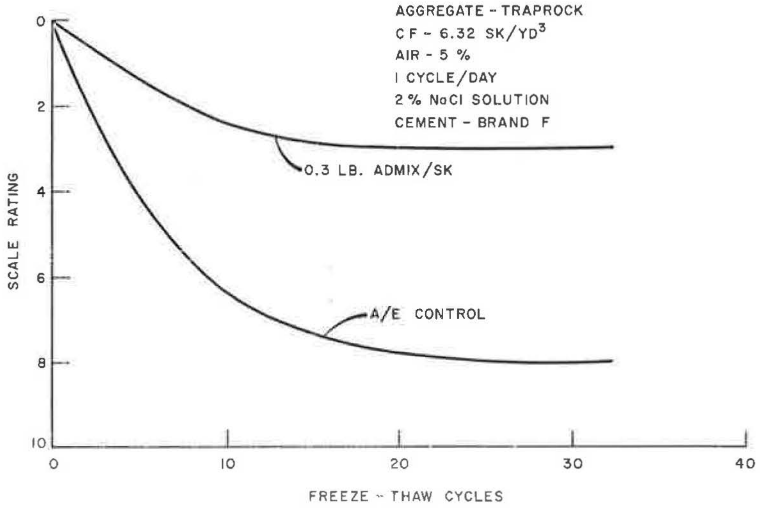

Figure 5. Scale rating vs freeze-thaw cycles.

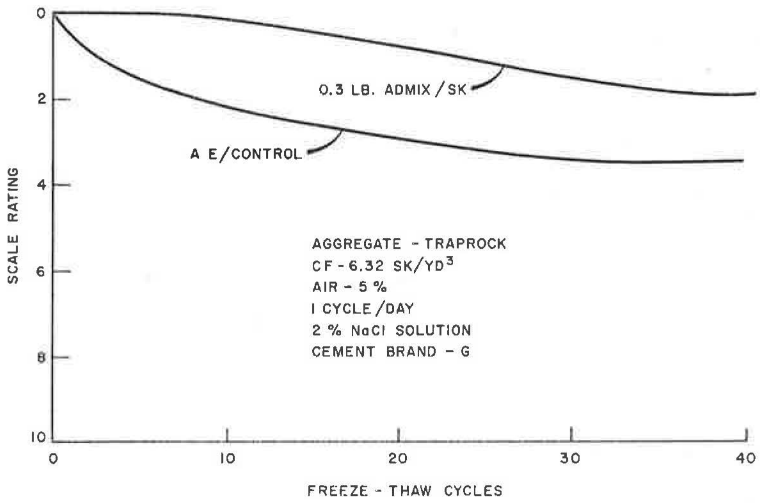

Figure 6. Scale rating vs freeze-thaw cycles.

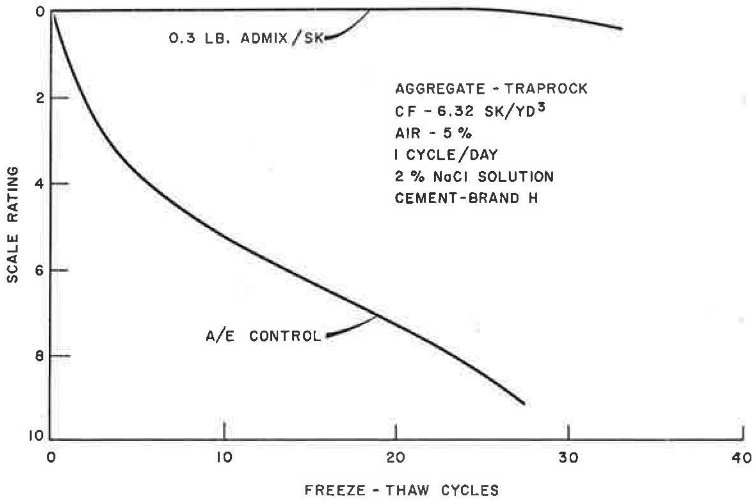

Figure 7. Scale rating vs freeze-thaw cycles.

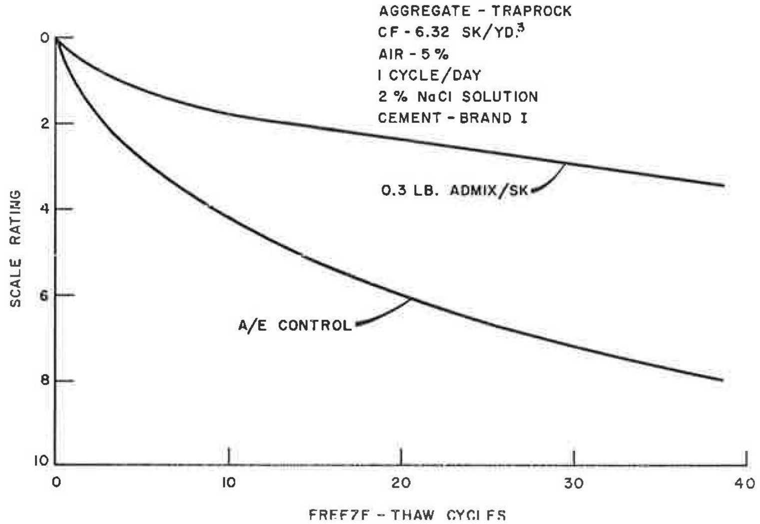

Figure 8. Scale rating vs freeze-thaw cycles.

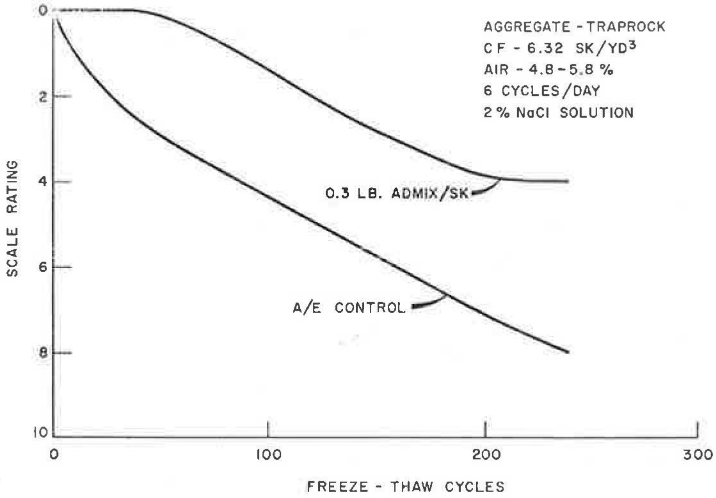

Figure 9. Scale rating vs freeze-thaw cycles.

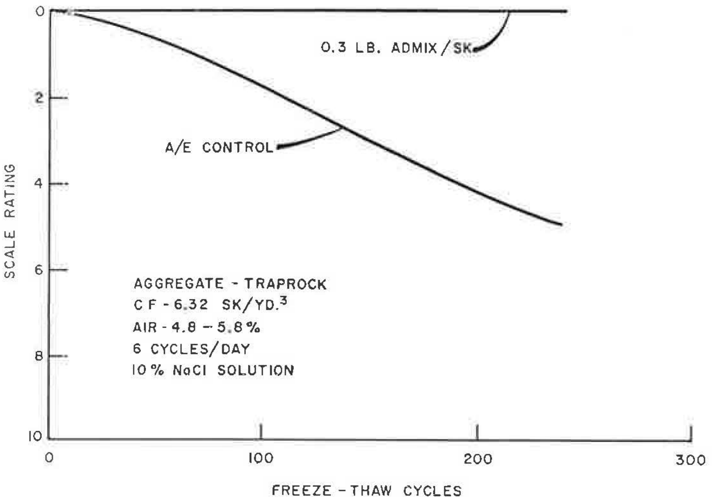

Figure 10. Scale rating vs freeze-thaw cycles.

results of these tests. The relative rates of deterioration are quite slow when the slabs are run with 10 percent salt solution on the surface, whereas deterioration under a 2 percent salt concentration is relatively rapid. The rate of concrete deterioration is much slower than with the slow-cycle test, indicating that a faster rate of freezing over a small temperature range (0 to 40 F) is less severe than a slower rate of freezing over a large temperature range (- 17 to + 70 F). In each of the freeze-thaw test methods evaluated in this report, the use of the silicone admixture has definitely improved the resistance of concrete to surface scaling over standard air-entrained concrete.

Effect of Admixture on Other Properties

Set Time—Proctor Penetrometer. —Incorporation of the silicone admixture extends the set time of concrete. A series of set times (Proctor set time, ASTM C-403) were run at 40, 60, and 100 F to compare the set times of air-entrained concrete with concrete containing the admixture (Figs. 11, 12, 13). Initial set times are delayed by several hours, depending on the ambient temperatures. Amines, hydroxides, carbonates, calcium chloride and other set accelerators have been evaluated in an effort to reduce the set time of the admixed concrete. At the present time there is no known accelerator that will shorten set time without a reduction of durability of the admixed concrete.

Slump Characteristics. —Another important property of concrete is the manner in which the consistency (as measured by the slump test) varies as a function of time. This was determined in the laboratory for both silicone admixed and air-entrained control concretes. The results show there is little difference between the admixed and air-entrained control concretes in the manner in which slump decreases over a period of time (Fig. 14). The Proctor set time test shows approximately a three- to five-fold increase in set time. The slump characteristics appear to be very similar to air-entrained concrete.

Compressive Strength. —When the silicone is admixed with concrete, the compressive strength is increased. Compressive strength tests were conducted on 4- by 8-in. cylinders in accordance with ASTM Method C-39. A normal distribution of data was observed. A typical S-shaped probability curve was generated when frequency vs 28-day compressive strength was plotted (Fig. 15). There is a 25 percent increase in mean compressive strength value with the silicone admixture. This compressive strength increase is not a result of a significant decrease in water to cement ratio.

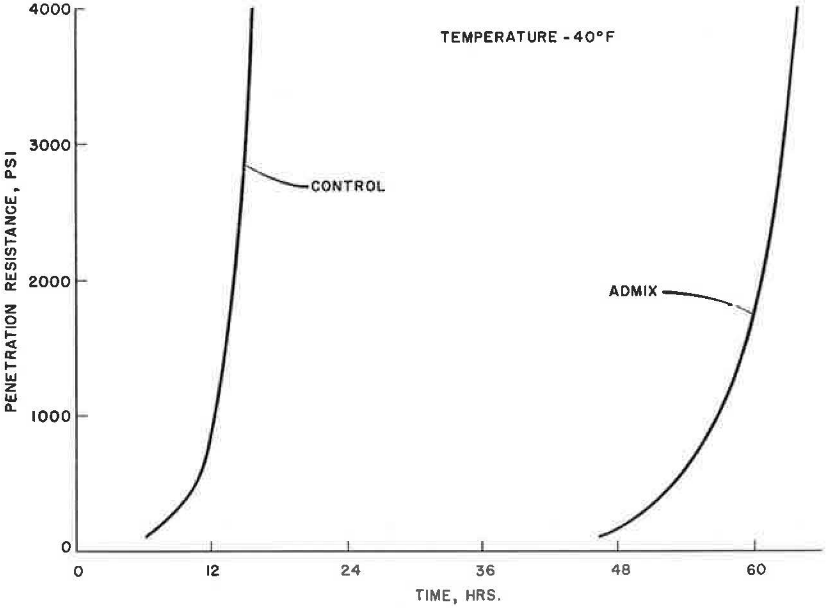

Figure 11. Penetration resistance vs time, hr.

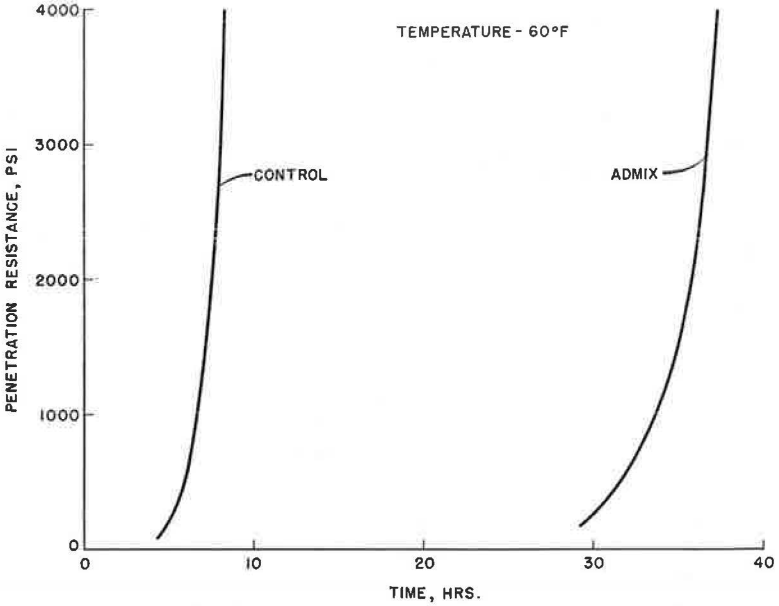

Figure 12. Penetration resistance vs time, hr.

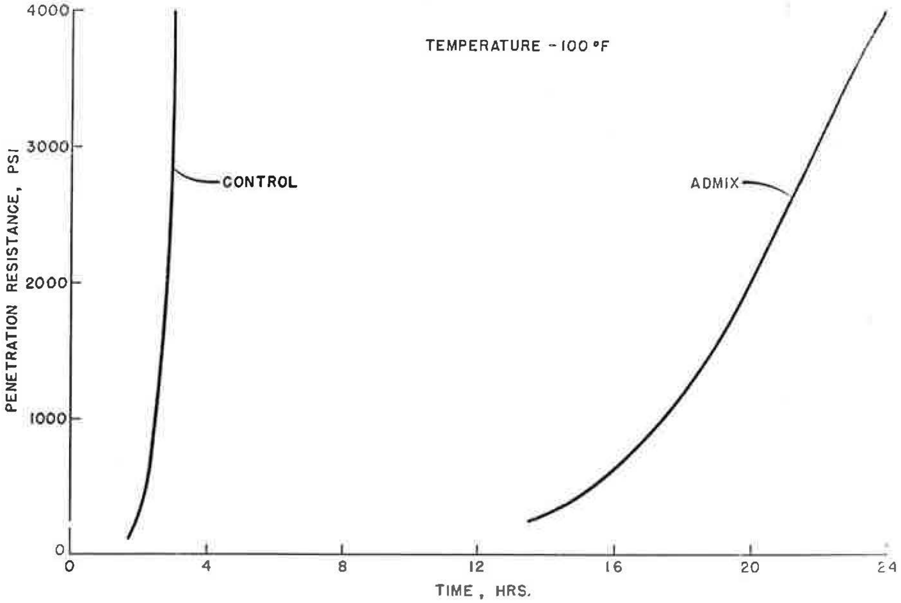

Figure 13. Penetration resistance vs time, hr.

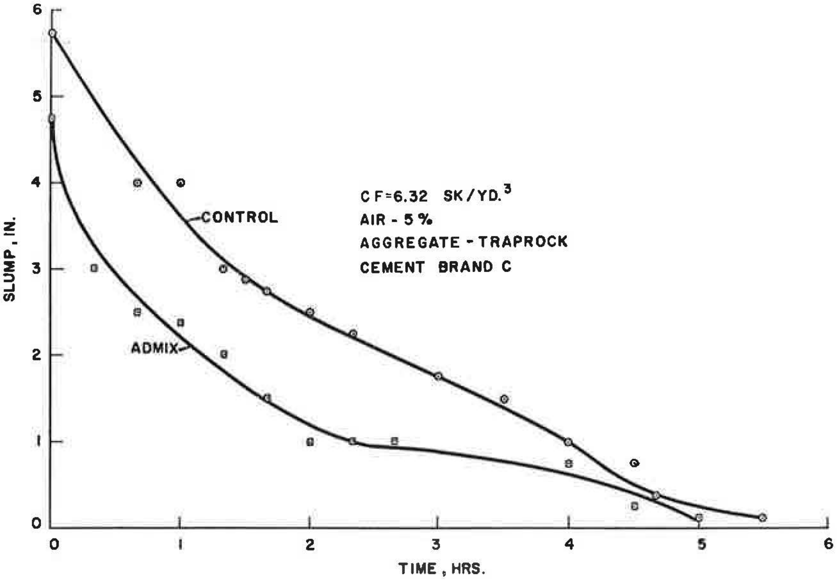

Figure 14. Slump vs time.

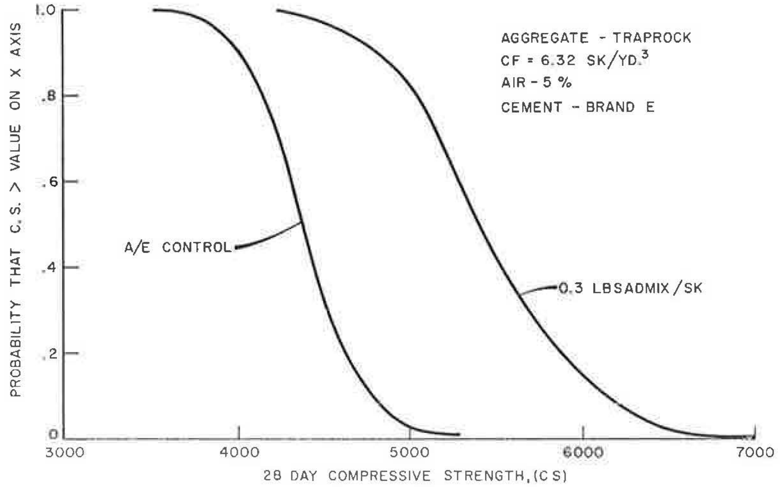

Figure 15. Probability vs 28-day compressive strength.

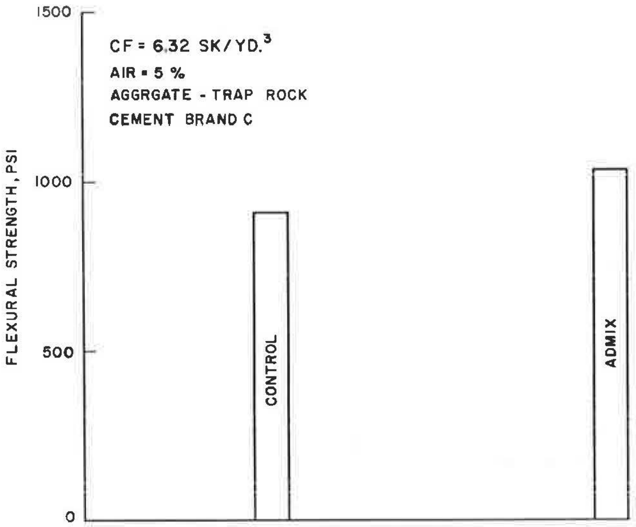

Figure 16. Flexural strength, control vs admix.

Flexural Strength. —Flexural strength is improved approximately 10 percent by the silicone admixture (Fig. 16).

Bond to Reinforcing Steel. —Bond to reinforcing steel was run according to ASTM C-234. Failure was taken at the maximum load the bond could support; slippage measurements were not made. Results of bond strength tests with admixed concrete are shown in Figure 17. The average increase in ultimate bond strength for admixed concrete is about 65 percent over an air-entrained control using a traprock aggregate system.

Shrinkage. —Shrinkage studies showed little difference between admixed and control samples (Table 6). The mortar bars were made in conformity with ASTM C-226. The shrinkage measurements were run for the first 28 days at 100 percent RH and for an additional 28 days at 50 percent RH.

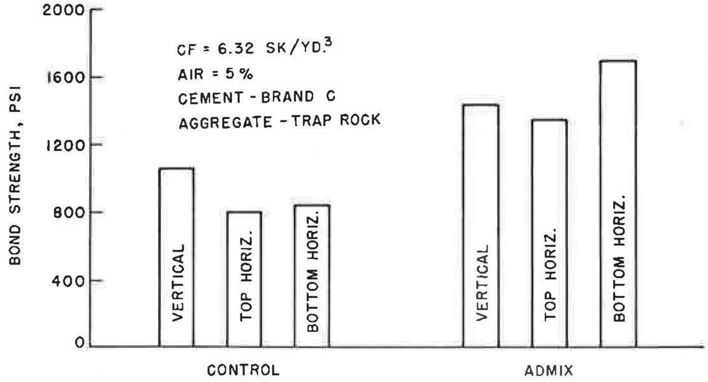

Figure 17. Bond strength, control vs admix.

Field Tests

During the summer of 1963 full-scale field trials were conducted. The first use of the silicone admixture in a significantly large test was at the Dow Corning plant at Elizabethtown, Ky. Over 100 yd of admixed concrete have been placed in areas such as shipping and receiving docks, tank farms, cooling water spray ponds, footings, and retaining walls. Air-entrained control areas have been placed in all cases in close proximity to the experiment.

Several field trials have been made on bridge decks, highway curbing and concrete guardrails. These tests were made in cooperation with various State highway departments. Each field trial has been thoroughly documented with air, slump, and strength measurements for each load of concrete used. In addition, freeze-thaw specimens have been made from each load of concrete and will be freeze-thaw tested in the laboratory.

Early strength figures look excellent on these field pours. Of course, durability of the concrete can only be conclusively determined after some appreciable service life. A complete report is not possible at this time.

TABLE 6

SHRINKAGE OF ADMIXED VS CONTROL CONCRETE

Aging Time (days)	Shrinkage (%)	
	Control	3% Admixture
(a) Cured at 100% RH		
2	+ 0.007	+ 0.009
7	+ 0.011	+ 0.022
14	+ 0.010	+ 0.024
28	+ 0.013	+ 0.030
(b) Cured at 50% RH[a]		
7	- 0.037	- 0.033
14	- 0.053	- 0.051
28	- 0.070	- 0.063

[a] After 28 days at 100% RH.

CONCLUSIONS

Concrete prepared under procedures outlined in this report and freeze-thaw tested with the described rapid-cycle and slow-cycle methods leads to the following conclusions:

1. The silicone, when admixed with concrete at the rate of 0.3 lb/sk, will cause average freeze-thaw durability increases of 120 percent in mixes carefully formulated with traprock aggregate and Long Island silica sand.
2. The primary freeze-thaw test used was a rapid-cycle procedure in 10 percent NaCl solution. This durability increase is of the same general order of magnitude when run in water or 2 percent NaCl solution.
3. The admixture increases the freeze-thaw durability of concrete made with different brands of cement, indicating that its function is not peculiar to any cement brand.
4. Tests of concrete at cement factors of 4, 5.5, 6.3, and 7 sk/yd indicate that the admixture improves freeze-thaw durability of concrete made with low, intermediate and high cement factors.
5. The type of deterioration produced by rapid-cycle tests in water and salt solutions

was a progressive erosion of the concrete surfaces determined by both a visual rating and a weight loss measurement. Structural failure did not occur when the admixture was used and appeared only on control concrete of air content less than 4 percent.

6. Slow-cycle scaling slab test results with 2 percent salt solution on the surface were in close agreement with rapid-cycle tests. The rate of deterioration was much more rapid due to the difference in testing procedure, but the type of deterioration was the same. Scaling slab tests show the silicone admixture increases freeze-thaw resistance when used with the different cement brands and at various cement factors.

Other properties of concrete affected by the silicone admixture are summarized as follows:

1. The set time, as measured by the Proctor penetrometer, is three to five times longer than a conventional concrete. Measurement of slump change with time and field experience indicates that admixed concrete has good handling properties.
2. Compressive strength advantages are not the same for all cement brands and factors tested, but in all cases a compressive strength increase can be expected from the admixed concrete.
3. The admixture increases bond to reinforcing steel approximately 65 percent and flexural strength by 10 percent.

Shrinkage does not appear to be greatly affected when the admixture is used.

REFERENCES

1. Verbeck, G. J., and Klieger, P., "Studies of 'Salt' Scaling of Concrete." HRB Bull. 150, pp. 1-13 (1957).
2. Public Roads, 28(7).

Discussion

P. SMITH and J. RYELL, respectively, Senior Materials Engineer (Concrete) and Concrete Testing Engineer, Materials and Research Division, Ontario Department of Highways.—Field trials are, of course, essential to any new concrete material or process. It may be worth mentioning a limited field trial undertaken in the fall of 1963, in co-operation with the authors, on a section of concrete curb and gutter at the junction of Highway 403 and the Queen Elizabeth Way some 30 west of Toronto, Ontario.

Approximately 1,000 lin ft of curb and gutter were split into random sections, alternating between the silicone admixture and the control air-entrained concrete in 5 cu yd loads of ready-mixed concrete. The concrete had a cement factor of 525 lb/cu yd, a slump of 2½ in. and used gravel aggregate of ¾-in. nominal maximum size and a well-graded natural sand.

The following was observed in this field trial, which might not be obvious from a laboratory evaluation:

1. The air content of the concrete after 15 min of mixing was approximately 5 percent; at the time of discharge this had dropped to less than 3 percent. Microscopic examination of the hardened concrete with 3 percent air content indicated that the spacing factor was slightly greater than 0.01. Thus, silicone concrete under field conditions might have a much less favorable air-void system than laboratory mixed concrete.
2. The mix containing the silicone admixture proved very difficult to finish in the curb and gutter section. This was no doubt partly due to the low air content, but the mix itself lacked the cohesiveness necessary for float finishing. The initial sand content was 40 percent; increasing this to 44 percent near the end of the trial section did not overcome this problem.

3. This particular silicone is a retarder. The initial set of the concrete (500 psi Proctor) occurred at 33½ hr, compared with 7 hr for the control mix. Considerations of extended curing, formwork pressures removal, opening to traffic, and possible damage by rain or freezing limit this type of concrete for some field uses.

4. The water reduction properties of the silicone admixture are approximately equal to that of a good lignosulfonate admixture with an air-entraining agent.

5. Four sets of standard test cylinders were made from both the silicone concrete and the control concrete. The control mix contained a lignosulfonate admixture; cement content of both mixes was 525 lb/cu yd concrete. The mean 28-day strength of the cylinders from the silicone mix was 7,070 psi; the mean 28-day strength of the control mix was 4,630 psi.

It may, therefore, be proper to ask if the promised advantages in strength gain and durability outweigh the problems encountered. Of the problems, those of retardation and difficulty of finishing might appear critical in acceptance of this class of admixture. Of the advantages, those of increased strength and durability might be considerable if, taking these into account, the concrete is no more expensive or any premium is worth the gains. Here the critical question must be—is normal air entraining, properly executed, inadequate to provide durability? In the discussors' experience it is adequate, but they wonder if the authors' experience is to the contrary. Problems with air entraining usually turn out to be traceable to acts of omission, such as not adding the agent or not checking the air content of the concrete at the time of placing. There seems to be no reason why a silicone admixture should not be just as vulnerable to a failing of man or dispenser.

B. C. CARLSON, R. C. HEDLUND, and D. F. CURTIS, Closure.—In the field trial in Ontario to which the discussors refer, there was, in some instances, a loss of entrained air from the time the concrete was mixed at the batch plant until it was received at the job site. Seven batches of admixed concrete were mixed and in four of these an air reduction of 2 percent or more was observed. However, a similar phenomenon was observed in one of the five air-entrained control batches in which a reduction of about 2 percent entrained air between first mixing and placing was observed. On three other field trials, no such occurrence was observed. These trials comprised a total of 43 batches of concrete whose total volume was 275 cu yd. In no case did the entrained air level fall below 4 percent.

Opinions on the difficulty of finishing the silicone admixed concrete have varied widely. On field trials, some finishers have reported that the admixed concrete was considerably stickier. The reverse observation was made on the part of other finishers who reported an improvement over the handling characteristics of ordinary air-entrained concrete. It is the opinion of the authors that a slight increase in stickiness does exist when the silicone admixture is added to the concrete.

Mr. Smith's Proctor penetrometer measurements concur exactly with those found by the authors. Laboratory and field trials have indicated, however, that extended curing is not required and that curing may be conducted with wet burlap, polyethylene film, or membrance curing compounds. The time of application of either burlap or polyethylene film is only slightly delayed and has been applied on bridge structures 4½ to 5 hr after placement of the concrete. On bridge superstructures, where the admixture is initially being tried, there has been no delay of formwork removal or opening to traffic. Forms are ordinarily not removed for at least 10 days and opening to traffic occurs normally at 28 days. Even at 4 days, the admixed concrete will equal or exceed the strength of normally air-entrained concrete; therefore, no delay because of strength considerations is encountered. If the admixed concrete is covered with burlap or polyethylene film, it will be no more subject to damage from rainfall than is ordinary air-entrained concrete because the covering of the admixed concrete can take place at about the same time as normal placements. Longer protection from freezing, particularly through the first and possibly the second night, may be required in the case of admixed concrete. This factor is presently under consideration and test by the authors.

The authors' observations are that the water reduction is approximately 4 percent when the silicone admixture is used. The increase in compressive strength observed on the Ontario test project was 52 percent when the admixture was employed in the concrete. Other documented field trials have shown increases in compressive strength of 38, 26 and 32 percent. The Ontario pour demonstrates that the admix does indeed produce a stronger concrete. In fact, the field trials have exceeded the predictions of the laboratory investigations wherein the mean improvement in compressive strength was computed to be 25 percent.

The authors do have personal knowledge of one case where concrete containing a sufficient amount of entrained air, measured before placing, and placed with the best possible workmanship has spalled. It is admitted that the failure may actually be due to lack of air in the surface of the hardened concrete. Assuming this to be the case, the premature failure of this concrete appears due to unknown phenomena and has little relationship to the amount of air-entraining agent present in the design. It is the authors' contention that the silicone admixture promotes durability in concrete by mechanisms apart from simple air entrainment. Whereas it is true that it will be no easier to control the amount of silicone in the concrete than it is the amount of air-entraining agent, it is believed that premature failures will be materially reduced because the concrete will be less subject to failures caused by mishandling of the material during placement.

Effect of Linseed Oil Coatings on Resistance of Concrete to Scaling

WILLIAM E. GRIEB and ROGER APPLETON
Respectively, Highway Research Engineer and Supervisory Engineering Technician, Materials Research Division, U. S. Bureau of Public Roads

•MANY STATE highway departments have been using surface coatings to protect concrete pavements from scaling and disintegration caused by the use of deicing chemicals. These coatings are often applied to concrete placed late in the fall to give it added protection and to compensate for the short aging period before the concrete is subjected to freezing. One of the materials often used for surface protective coatings is linseed oil.

The specifications governing the use of this material vary. Some States specify its use as an emulsion, whereas others require that it be diluted with mineral spirits when applied. One or two applications of the linseed oil may be required.

Tests were made in the laboratory of the U. S. Bureau of Public Roads to determine whether the use of the surface treatments of linseed oil are beneficial in preventing scaling of the concrete.

MIX DATA

Four different mixes were used in these tests: (a) non-air-entrained concrete with 2½-in. slump, (b) non-air-entrained concrete with 6-in. slump, (c) air-entrained concrete with 2½-in. slump, and (d) air-entrained concrete with 6-in. slump. The mix data are given in Table 1.

MATERIALS

All mixes used a type I portland cement with an equivalent alkali content of 0.6 percent, a siliceous sand with a fineness modulus of 2.75, and a crushed limestone uniformily graded from 1 in. to No. 4. When needed, a commercially available aqueous solution of neutralized Vinsol resin was used to entrain air. The linseed oils used met Federal specifications.

CURING

The test specimens were 16- by 24- by 4-in. slabs with a raised edge or dam around the perimeter of the top surface. The specimens were similar to those described in a recent report of the Bureau (1). The slabs were cast in watertight molds with metal bases. The top surfaces of the slabs were screeded with a wooden straightedge and about 3 hr after molding were given a light broomed finish, similar to that given a concrete pavement. All specimens were molded, finished and cured in as nearly the same manner as possible. All were cured in the molds with wet burlap for 2 days and ponded for 12 days. They were then dried in laboratory air at 70 to 80 F and 30 percent RH for 7 days before application of the surface treatments. After the surface treatments were applied, the slabs were kept in laboratory air for 7 to 14 days and then placed in the outdoor exposure area. When two applications of a surface treatment were used, they were applied 24 hr apart. All specimens were from 28 to 35 days old when they were stored in the exposure area; the first natural freeze occurred 3 days later.

Paper sponsored by Committee on Effect of Ice Control.

TABLE 1

MIX DATA[a]

Proportions by Dry Weight (lb)	Cement Content (sk/cu yd)	Water Content (gal/sk)	Slump (in.)	Air Content ($)	Plastic Concrete (lb/cu ft)
94 - 205 - 305	6.2	5.5	2.6	2.0	149.1
94 - 205 - 305	6.1	6.2	6.0	1.4	148.7
94 - 190 - 305	6.2	5.2	2.7	5.0	145.9
94 - 190 - 305	6.1	5.9	6.2	5.1	144.2

[a] Materials used: type I portland cement, crushed limestone 1 in. max, and siliceous sand (F. M. 2.75).

SURFACE TREATMENTS

Ten identical slabs were made for each of the four mixes. Two slabs for each mix were given the following surface treatments: (a) no surface treatment (control slabs), (b) two applications of boiled linseed oil, (c) two applications of raw linseed oil, (d) one application of boiled linseed oil, and (e) two applications of linseed oil emulsion. The first coating for both the boiled and raw linseed oil was applied as a mixture of equal parts by volume of linseed oil and mineral spirits at a rate of 1 gal/40 sq yd of surface. The second coat was applied as undiluted linseed oil at a rate of 1 gal/67 sq yd.

The linseed oil emulsion used consisted of 1 part boiled linseed oil, 1 part kerosene, 3 parts water plus a small amount of trisodium phosphate, and a small amount of non-detergent soap powder as an emulsifying agent. The emulsion was applied at a rate of 1 gal/10 sq yd of surface for each application.

Observations were made of the time necessary for the various coatings to be absorbed by the concrete. The boiled and raw linseed oils diluted with mineral spirits were absorbed in about 30 min, whereas the linseed oil emulsion was absorbed in about 100 min. The rate of absorption varied as the mix of concrete on which the material was applied.

The air-entrained concrete with high slump absorbed the coatings more rapidly than the other mixes. The non-air-entrained concrete with high slump absorbed them the next fastest, followed by the air-entrained low slump concrete, whereas the non-air-entrained low slump concrete took the longest to absorb the coatings. A second coat took longer to absorb into the concrete than the first coat. This information may be of value as a guide for the use of these materials in the field.

TESTING PROCEDURE

Each evening when freezing was expected, the top surface of each slab was covered with ¼ to ½ in. water. The next morning, flake calcium chloride was spread uniformily over the ice-incrusted surface at a rate of about 2.4 lb/sq yd of surface. This rate of application is greater than would be used in the field but is that used on other research projects. After the ice melted, the surface was washed and covered with fresh water.

The specimens were examined periodically and rated by visual observations according to the amount and depth of the scaling. The numerical ratings are as follows:

0 = no scale;
1 = scattered spots of very light scale;
2 = scattered spots of light scale with mortar surface above coarse aggregate removed;
3 = light scale over about one-half of the surface;
4 = light scale over most of the surface;
5 = light scale over most of the surface, with a few moderately deep spots where the mortar surface was below the upper surface of the coarse aggregate;
6 = scattered spots of moderately deep scale;
7 = moderately deep scale over one-half of the surface;
8 = moderately deep scaling over entire surface;
9 = moderately deep scaling and scattered spots of deep scale with the mortar surface well below the upper surface of the coarse aggregate; and
10 = deep scale over entire surface.

A rating of 5 or more would indicate significant or major scaling. The ratings given the slabs were based on the judgment of different observers at the various times that the observations were made, which accounts for occasional slight reversals.

These specimens were in the outdoor exposure area for two winters and had a total of 105 cycles of freezing and thawing (45 cycles the first winter and 60 cycles the second). Previous tests have shown that exposure for two winters is sufficient to indicate the resistance of concrete test specimens to scaling caused by the use of calcium chloride.

TEST RESULTS

The average ratings of the slabs after 10, 20, 30, 45, 60, 80, and 105 cycles of freezing and thawing are given in Table 2. Slabs of non-air-entrained concrete with low slump and no surface coatings had a rating of 10 after 30 cycles of freezing and thawing. The tests on these slabs were discontinued. None of the slabs which had the linseed oil surface coating showed any sign of scaling at that time. At 45 cycles, scaling had started on the slabs with one coat of boiled linseed oil and those with the two coats of the emulsion. At 105 cycles the slabs with 2 coats of the emulsion showed severe scaling over part of the surface, those with one coat of boiled linseed oil showed light scaling over the entire surface, those with two coatings of boiled or raw linseed oil showed very little scaling.

For the non-air-entrained concrete with high slump, the slabs with no surface treatment were completely scaled after only 20 cycles of freezing and thawing. For this same number of cycles, the slabs with one coat of boiled linseed oil and those with two coats of the emulsion had ratings of 4 and 2, respectively; those with two coatings of raw and boiled linseed oil showed no signs of scaling. After 45 cycles, deep scaling over the entire surface was found on the slabs with one coat of boiled linseed oil. Those with two coats of the emulsion had a rating of 9 after 60 cycles. After 105 cycles, the slabs with two coats of the boiled linseed oil had an average rating of 2 and those with two coats of raw linseed oil an average rating of 4. There was a marked difference in the amount of scaling between the two slabs given the two coats of the raw linseed oil. One slab had virtually no scaling, whereas the other was severely scaled over a portion of its surface. No reason can be given for the difference in performance of these supposedly identical slabs.

All slabs prepared with air-entrained concrete with low slump showed good resistance to scaling. After 105 cycles of freezing and thawing, the slabs with two coatings

TABLE 2

RATING OF SLABS[a]

Surface Coatings	Slump (in.)	Air Content (%)	Rating After Cycles Shown						
			10	20	30	45	60	80	105
(a) Non-Air-Entrained Concrete									
None	2.6	2.0	4	9	10	—	—	—	—
2 coats boiled linseed oil	2.6	2.0	0	0	0	0	0	0	1
2 coats raw linseed oil	2.6	2.0	0	0	0	0	1	1	1
1 coat boiled linseed oil	2.6	2.0	0	0	0	1	2	2	4
2 coats linseed oil emulsion	2.6	2.0	0	0	0	2	4	5	6
None	6.0	1.4	8	10	—	—	—	—	—
2 coats boiled linseed oil	6.0	1.4	0	0	1	1	1	1	2
2 coats raw linseed oil	6.0	1.4	0	0	1	1	3	4	4
1 coat boiled linseed oil	6.0	1.4	1	4	9	10	—	—	—
2 coats linseed oil emulsion	6.0	1.4	0	2	5	7	9	9	9
(b) Air-Entrained Concrete									
None	2.7	5.0	0	0	0	0	1	1	3
2 coats boiled linseed oil	2.7	5.0	0	0	0	0	0	0	1
2 coats raw linseed oil	2.7	5.0	0	0	0	0	0	0	1
1 coat boiled linseed oil	2.7	5.0	0	0	0	1	2	3	4
2 coats linseed oil emulsion	2.7	5.0	0	0	0	0	1	2	3
None	6.2	5.1	0	0	0	0	3	4	6
2 coats boiled linseed oil	6.2	5.1	0	0	0	0	0	0	2
2 coats raw linseed oil	6.2	5.1	0	0	0	1	3	3	4
1 coat boiled linseed oil	6.2	5.1	0	2	4	5	6	6	5
2 coats linseed oil emulsion	6.2	5.1	0	1	1	1	4	4	5

[a] Each value average for two test specimens.

NO SURFACE TREATMENT (RATINGS 10 & 10)

2 COATS BOILED LINSEED OIL (RATINGS 1 & 1)

2 COATS RAW LINSEED OIL (RATINGS 1 & 1)

1 COAT BOILED LINSEED OIL (RATINGS 3 & 4)

2 COATS LINSEED OIL EMULSION (RATINGS 7 & 6)

Figure 1. Effect of linseed oil surface treatments on scaling: 105 cycles, slump 2.6 in., air 2.0 percent.

NO SURFACE TREATMENT (RATINGS 10 & 10)

2 COATS BOILED LINSEED OIL (RATINGS 3 & 1)

2 COATS RAW LINSEED OIL (RATINGS 6 & 1)

1 COAT BOILED LINSEED OIL (RATINGS 10 & 10)

2 COATS LINSEED OIL EMULSION (RATINGS 9 & 9)

Figure 2. Effect of linseed oil surface treatments on scaling: 105 cycles, slump 6.0 in., air 1.4 percent.

NO SURFACE TREATMENT (RATINGS 3 & 3)

2 COATS BOILED LINSEED OIL (RATINGS 1 & 1)

2 COATS RAW LINSEED OIL (RATINGS 1 & 1)

1 COAT BOILED LINSEED OIL (RATINGS 4 & 3)

2 COATS LINSEED OIL EMULSION (RATINGS 3 & 3)

Figure 3. Effect of linseed oil surface treatments on scaling: 105 cycles, slump 2.7 in., air 5.0 percent.

NO SURFACE TREATMENT (RATINGS 5 & 6)

2 COATS BOILED LINSEED OIL (RATINGS 1 & 2)

2 COATS RAW LINSEED OIL (RATINGS 3 & 4)

1 COAT BOILED LINSEED OIL (RATINGS 6 & 4)

2 COATS LINSEED OIL EMULSION (RATINGS 5 & 5)

Figure 4. Effect of linseed oil surface treatments on scaling: 105 cycles, slump 6.2 in., air 5.1 percent.

of the boiled or raw linseed oils showed very little scaling and were rated as 1. The average rating for the other slabs was 3 or 4, including both the treated and the untreated or reference slabs.

The slabs prepared with air-entrained concrete and high slump showed good to fair resistance to scaling. The slabs with two coatings of the boiled linseed oil had the best resistance, having a rating of 2 after 105 cycles. Those with two coatings of the raw oil had a rating of 4 after 105 cycles. These was little difference in the average ratings of the other slabs; all were 5 or 6.

Photographs of all slabs after 105 cycles of freezing and thawing or when they were given a rating of 10 are shown in Figures 1 through 4. These figures also show the final rating of each slab. There was, in general, good uniformity between the two slabs from the same mix given the same surface treatment. Only in the one case, previously mentioned, was the difference in ratings between the two similar slabs greater than 2. In over half the cases, the ratings given were the same.

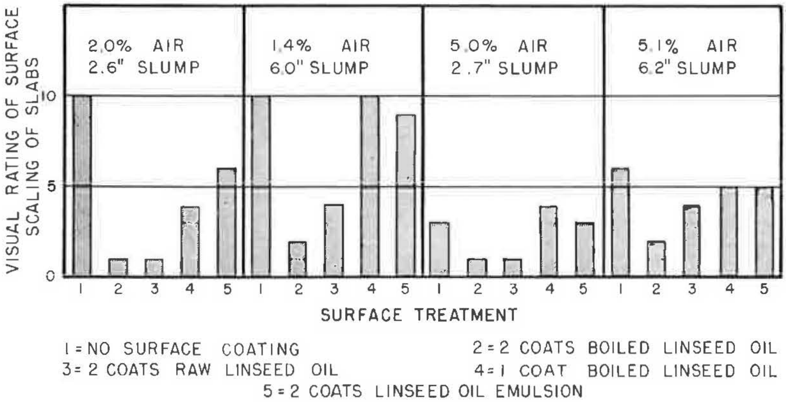

Figure 5. Effect of linseed oil surface coatings on scaling after 105 cycles of freezing and thawing with $CaCl_2$.

SUMMARY

A summary of the ratings of the slabs after 105 cycles of freezing and thawing is shown in Figure 5. For both the low and the high slump non-air-entrained concretes, all linseed oil surface treatments were beneficial in preventing or delaying scaling caused by the use of deicing chemicals. Applications of two coats of either the boiled or the raw linseed oil were the most beneficial surface treatments. With one exception, the slabs given two coats of boiled or raw linseed oil were the only non-air-entrained concrete specimens that did not show significant scaling after 105 cycles.

For the air-entrained concrete of low or high slump, the two-coat application of either boiled or raw linseed oil was the only surface treatment effective in preventing or delaying scaling. The other surface treatments were of little or no benefit. For the low slump air-entrained concrete, non of the slabs, including those with no surface treatment, showed significant scaling. All slabs prepared from the high slump air-entrained concrete except those given two coats of boiled or raw linseed oil showed significant scaling.

The slabs treated with two coats of boiled linseed oil were equally or more resistant to scaling than those treated with two coats of raw linseed oil.

Greater resistance to scaling was furnished by the low slump concrete than by the corresponding high slump concrete, and greater resistance was furnished by the air-entrained concrete than by the corresponding non-air-entrained concrete.

REFERENCE

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).

Application of Differential Thermal Analysis in Cement Research

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Differential thermal analysis (DTA) has recently attained increasing importance as a research tool in cement chemistry. DTA is normally used in identifying various materials but could also be employed to follow reactions by heating the reactants gradually to elevated temperatures. Use of sensitive equipment and proper calibration facilitate quantitative estimation of materials. Certain poorly crystallized compounds not easily identifiable by x-ray diffraction give characteristic thermal peaks.

This review presents the application of DTA to portland cement. Other cements are included to illustrate the importance of DTA to an understanding of the chemistry of cement in general and also of the potentialities of the method itself.

•THE TECHNIQUE of differential thermal analysis (DTA) is widely applied in clay mineralogy, but only recently has it been extended to other fields. The method consists of measuring the heat changes associated with physical or chemical transformations occurring during the gradual heating of a substance. Thermal changes, such as dehydration, crystalline transition, lattice destruction, oxidation and decomposition, are generally accompanied by an appreciable rise or fall in temperature and are amenable to DTA investigation. The DTA technique has found application in diverse fields such as criminology, pyrotechnics, catalysis, coal chemistry, polymer systems, radioactivity, soap and lubricating systems and will continue to be introduced to various branches of study.

The DTA method had its origin in 1887 when Le Chatelier applied thermal analysis to the study of the constitution of clays (1 - 4). However, although one of the pioneers in the field of cement chemistry, he did not realize the potentialities of the method to the study of cements. Kalousek et al. (5) were probably first to introduce DTA in cement chemistry. The usefulness of the method was realized and discussed at the Third International Symposium on the Chemistry of Cements held in London in 1952, and since then several papers have appeared dealing with the DTA of cementitious materials. The remarks made by R. H. Bogue (6) at the London symposium are significant:

> Our ability to detect and measure small temperature differentials has been greatly extended by new electronic instruments capable of rapid and automatic recording of minute changes in energy levels. With these instruments, differential thermal-analytical methods are replacing the older quenching techniques for following phase relations with the assurance that energy changes too small or too rapid otherwise to be observed will be identified.

Between 1952 and 1960, increasing attention was paid to the application of DTA in cement chemistry and at the Fourth International Symposium on the Chemistry of Cement, held in 1960, several investigators interpreted their results through thermographic analysis.

Paper sponsored by Committee on Basic Research Pertaining to Portland Cement and Concrete.

DESCRIPTION OF THE METHOD

Essentially the DTA equipment consists of a furnace, a temperature regulator, a specimen block, thermocouples, and a temperature-recording system. Several types of apparatus are in use. Refinements have been suggested from time to time to give greater accuracy in results and to widen the scope of the method.

The sample to be studied is placed in one of the cavities of the specimen block (Fig. 1). In the second cavity is placed calcined alumina, α-Al_2O_3, which does not experience any thermal change within the temperature range usually used in the study. Two thermocouples, constituting the differential thermocouple, are connected as shown. In the third cavity of the block a separate thermocouple is embedded to measure the temperature of the specimen. The temperature can also be measured by connecting the thermocouple ends a-b from the inert material as shown in Figure 1b.

The block with the specimen to be studied and inert material, α-Al_2O_3, is placed in a furnace and the temperature is raised at a uniform rate. The differential couple records zero potential difference when the specimen is not undergoing any thermal change. During a thermal transformation, the increase or decrease in the temperature of the specimen, relative to that of the inert material, will depend on the exo- or endothermal character of the change. With the completion of the thermal change, the specimen usually reattains the temperature of the inert material. In some cases, the zero line shows a drift after a thermal transformation and is attributed to the differences in thermal characteristics between the specimen and the inert material. The differential temperature is recorded as a function of time or the temperature of the specimen block. In the thermograms, usually the differential temperature, ΔT, and the block temperature, T, are recorded or plotted in such a manner that the endothermic peaks are shown downwards and the exothermic peaks, upwards with respect to the baseline, $\Delta T = 0$. The details of the DTA technique, theory, and varied applications are discussed in various sources (7 - 14).

The discussion herein pertains mainly to the application of DTA in the field of portland cement. The inclusion of the related work was necessitated to indicate its importance to an understanding of the chemistry of cement and of the potentialities of the method itself.

PORTLAND CEMENT CLINKER

Raw Materials

Portland cement is formed by firing chalk, limestone, marl or marine shells with shale or clay or other siliceous materials to a temperature of 1400 to 1500 C, mixing the resulting sintered clinker with 4 to 5 percent gypsum, and grinding to a very fine powder of average diameter of $10\ \mu$. In some cement plants gypsum is replaced by anhydrite or a mixture of anhydrite and gypsum.

In the formation of cement clinker, the clay contributes SiO_2, Al_2O_3, and, possibly, iron, alkalies and alkaline earths,

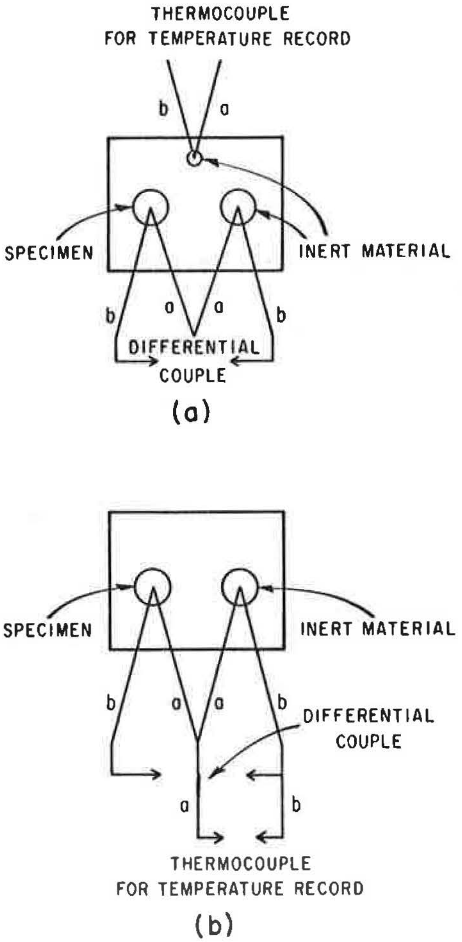

Figure 1. Specimen block with thermocouple connections.

depending on the clay mineral composition. More than 5 percent MgO in cement causes unsoundness of concrete. Consequently, clay minerals rich in Mg, such as attapulgite, sepiolite and chlorite, do not make suitable raw materials for cement manufacture. Kaolinite comprises mainly SiO_2 and Al_2O_3 and, hence, is suitable as a raw material, especially for the manufacture of white portland cement. Illite and montmorillonite clay minerals normally form suitable raw materials. Schweite (15) observed that kaolinite is much more suitable for wet manufacturing process because it exhibits better burning characteristics and produces less dusting during grinding. Caution should be exercised in choosing a suitable lime source. If the original limestone contains MgO in the form of dolomite, the resultant cement will be unsound.

The application of DTA to the examination of raw materials for cement production should prove useful in assessing their suitability. Figure 2 shows typical thermograms of some raw materials. The temperature of the peak, the endo- or exothermal character, the intensity and other general characteristics are used to identify each material.

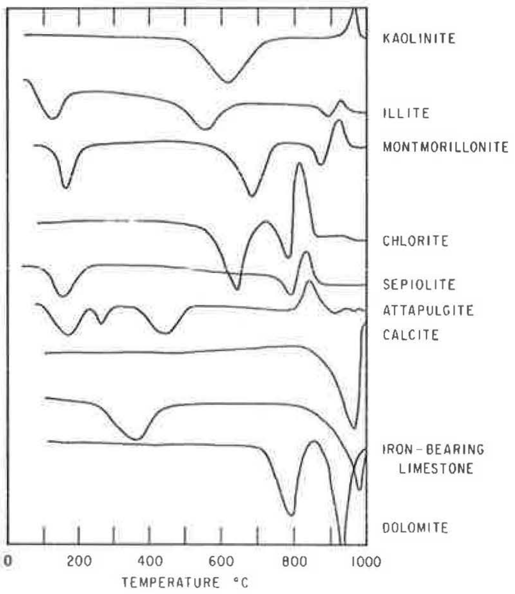

Figure 2. DTA of some raw materials for manufacture of cement.

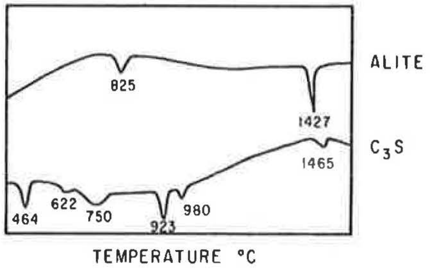

Figure 3. Thermograms of alite and pure tricalcium silicate.

Nature of Cement Clinker

Portland cement clinker contains a mixture of four major phases, C_3S, β-C_2S, C_3A and a ferrite phase extending in composition from C_4AF to C_6AF_2 (16). (Symbols used are defined as follows: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO, K = K_2O, N = Na_2O and H = H_2O.) The C_3S phase contains some Al and Mg in solid solution, whereas the C_2S phase contains some K_2O and the C_3A phase, some Na_2O. The clinker has a glassy phase ranging from 2 to 20 percent, and frequently the greater proportion of C_3A and ferrite exists in this phase. According to some workers there is essentially no glassy phase in the clinker.

Le Chatelier designated the predominant component of portland cement clinker as "alite" with a probable formula, C_3S. Nurse and Welch (17) carried out DTA of pure C_3S, alite and a cement clinker rich in alite. In Figure 3 are shown the DTA of pure C_3S and alite in the range 150 to 1500 C as obtained by them. Six endothermal transformations are observed in pure C_3S. The peak at 464 C is due to loss of water of hydration from the surface of CaO grains and those at 622 and 750 C are due to $\beta \rightarrow \alpha'$ and $\gamma \rightarrow \alpha'$ transformations of C_2S, respectively. The peak at 1465 C is attributed to $\alpha' \rightarrow \alpha$ transformation. The thermal effects at 923 and 980 C for C_3S are more speculative and are ascribed to either, triclinic $\underset{\longrightarrow}{923\ C}$ monoclinic $\underset{\longrightarrow}{980\ C}$ trigonal or triclinic → trigonal → trigonal + rotation of anions. Synthetic alite ($C_{54}S_{16} \cdot M \cdot A$) exhibits two endothermic peaks at 825 and 1427 C. The peak at 825 C is due to monoclinic → trigonal transformation and the higher temperature endothermic peak is due to transformation in C_3S. A cement containing 60 percent C_3S, however, indicated no thermal transformations that could be ascribed to C_3S. The metastable inversions at 923 and 980 C in pure C_3S and at 850 C in alite reported by Nurse and Welch were confirmed by others (18, 99, 100).

There are four polymorphic forms of C_2S (γ, β, α' and α) stable in the range 0 to 1600 C. Only the β and, occasionally, the γ forms are likely to occur in the cement clinker. Minute quantities of α' form were observed under exceptional conditions (19). It should also be noted that α, α', and β forms are not stable at room temperature in absence of stabilizers. DTA has successfully provided the accurate inversion temperatures of the four forms of C_2S and has played an important role in establishing the interrelationship of the various forms (20). The quenching technique would not prove useful in this investigation because neither the α nor the α' form is stable at room temperature. Newman and Wells and Vasenin (21, 22) studied the transformations in C_2S, and the work carried out at the British Building Research Station has provided accurate inversion points of various forms of C_2S (23). The results are presented in Figure 4. Curve A shows two peaks obtained by heating γ-C_2S. At first sight these transformations could be mistaken for $\gamma - \beta$ and $\gamma \rightarrow \beta$ transformations. A better interpretation is based on the cooling curve of the same substance. Curve B shows three peaks corresponding to three inversions. If the cooling is stopped at about 600 C and heating restarted, curve C results instead of curve A. Curve A is reproducible if the material is allowed to cool to room temperature before heating is re-started. The interpretation of these curves is as follows: on heating the γ-C_2S, the phase change is in the sequence $\gamma \rightarrow \alpha' \rightarrow \alpha$, the β-form appearing only on the cooling cycle below 600 C; the $\beta \rightarrow \gamma$ inversion takes place on slow cooling or $\beta \rightarrow \alpha' \rightarrow \alpha$ inversion on heating. These results were confirmed by de Keyser (24).

The stabilizing influence of barium orthosilicate on C_2S was studied by DTA. C_2S treated with various amounts of the stabilizing agent indicated absence of $\gamma \rightarrow \alpha'$ inversion on addition of more than 10 percent (25).

Systems With CaO, Al_2O_3, SiO_2 and Fe_2O_3

The thermal reactions in the binary, ternary and quaternary systems involving CaO, SiO_2, Fe_2O_3, and Al_2O_3 are of great importance in the study of the chemistry of cement clinker. Rapid heating of these mixtures in a thermal analyser results in the appearance of thermal inflections caused by the formation of various products.

Budnikov and Sologubova (26) applied DTA to the study of the reaction between kaolin and calcium carbonate in the production of white cement. The formation of $CaO \cdot Al_2O_3$ was indicated by an exothermal peak above 1000 C. The mortars cured for 28 days exhibited an endothermic effect at 320 to 340 C which was attributed to dehydration of $2CaO \cdot Al_2O_3 \cdot 7H_2O$. The formation of tricalcium silicate by the interaction of calcium carbonate and silica has been studied by DTA (27). De Keyser has done extensive work

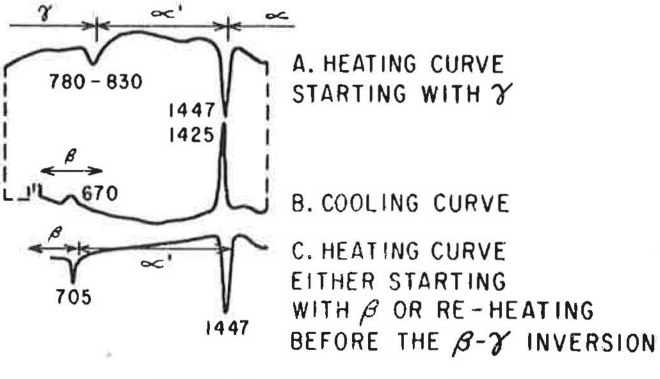

Figure 4. Inversions in C_2S.

on various oxide systems. He heated a mixture of SiO_2-CaO-Al_2O_3 and also a CaO-kaolin mixture between 1000 and 1400 C and studied the reaction by DTA (28). Between 1200 and 1300 C, the reaction was controlled by the diffusion of oxides. In CaO-kaolin, gehlenite (C_2AS) was found to form between 900 and 1000 C, contrary to the results of Budnikov and Sologubova (26). At higher temperatures CA converted to C_5A_3. A mixture of $Ca(OH)_2$ and SiO_2, when heated rapidly in a thermal analyser, exhibited several inflections in the thermograms. Samples were withdrawn at various temperatures corresponding to thermal inflections and examined by x-ray diffraction. Three endothermic peaks at 148, 490 and 555 C and three exothermic peaks at 800, 846 and 970 C were observed. The x-ray results showed at about 480 C the presence of γ-C_2S which converted to β-C_2S at 960 C.

Further work by de Keyser (29) on the system 2 CaO , Fe_2O_3, 6 CaO + Al_2O_3 + 2 Fe_2O_3, 4 CaO + Al_2O_3 + Fe_2O_3 and 6 CaO + 2 Al_2O_3 + Fe_2O_3 in the range 500 to 1300 C indicated that all these mixtures form 2 CaO· Fe_2O_3 from 800 C and CaO·Fe_2O_3 at higher temperatures. At still higher temperatures, CaO· Fe_2O_3 reacted, with CaO to form 2 CaO· Fe_2O_3 with the maximum rate of formation at 1200 C. For mixtures containing Al_2O_3, 3 Al_2O_3· 5 CaO was the product between 1000 to 1250 C.

A systematic work has been carried out by Barta and co-workers (101-104) to follow the reaction when different mixtures of CaO, Al_2O_3, SiO_2 and Fe_2O_3 are gradually heated in the DTA furnace. DTA gives valuable information on the temperature of transformations, though the values may be different from those obtained from equilibrium studies. Some of the results obtained are shown in Figures 5 to 8.

Figure 5 shows the DTA behavior of 3 CaO + SiO_2 and also the effect of additions of Al_2O_3 and mixtures of Al_2O_3 + Fe_2O_3 on the temperature of formation of C_3S. The exothermic peak at 1450 C indicates the formation of C_3S. The peak temperature decreases to 1380, 1350 and 1320 C with additions of 5 percent Al_2O_3, 2 percent Al_2O_3 + 2 percent Fe_2O_3 and 5 percent Al_2O_3 + 5 percent Fe_2O_3, respectively.

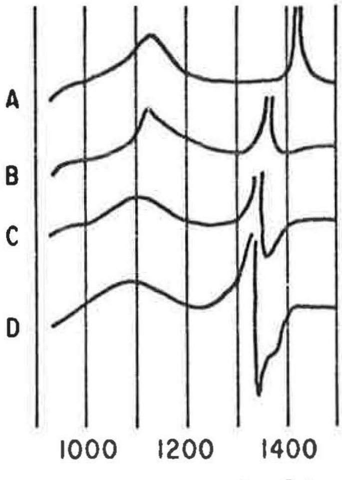

Figure 5. Thermograms of 3 CaO + SiO_2 : A, 3 CaO + SiO_2 ; B, with 5% Al_2O_3 ; C, with 2% Al_2O_3 + 2% Fe_2O_3 ; D, with 5% Al_2O_3 + 5% Fe_2O_3 .

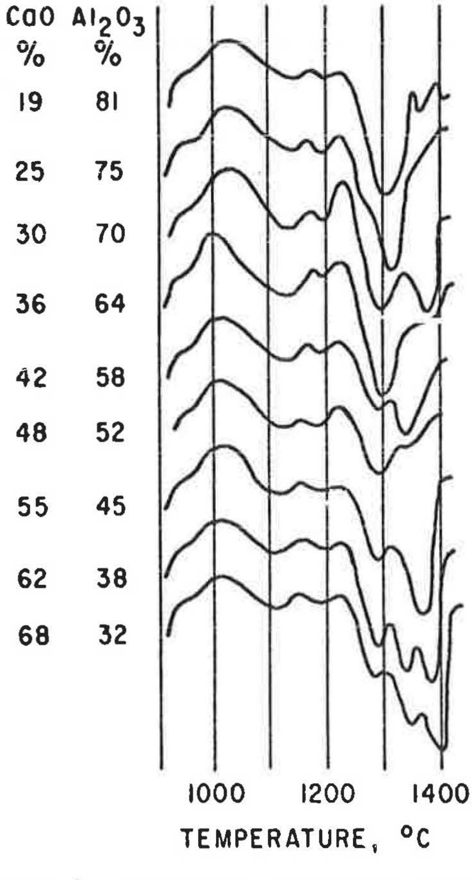

Figure 6. Thermograms of mixtures of CaO and Al_2O_3 .

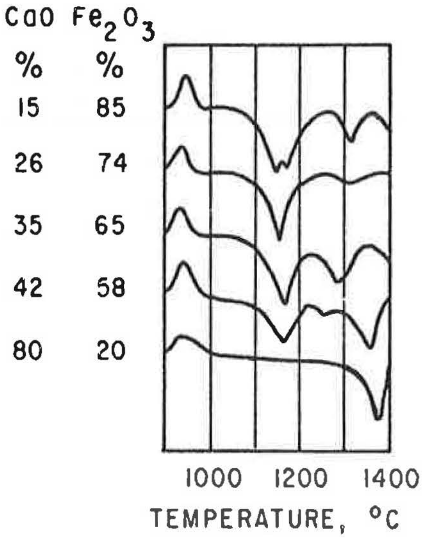

Figure 7. Thermograms of mixtures of CaO and Fe_2O_3.

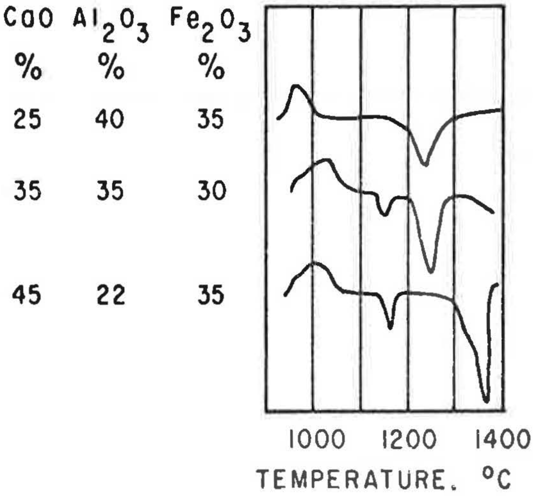

Figure 8. Thermograms of ternary mixture containing CaO, Al_2O_3 and Fe_2O_3.

In Figure 6, the DTA curves of different proportions of CaO in Al_2O_3 are shown. The exothermic effect at 950 to 1000 C is attributed to a simultaneous formation of CA and $C_{12}A_7$. The dip at 1170 C represents the change of γ-Al_2O_3 to α form and the other at 1200 C corresponds to the beginning of formation of C_3A. The endothermic peak at 1300 C indicates melting in the system. Other endothermic effects at higher temperatures are not discussed.

Reactions of different mixes of CaO and Fe_2O_3 are represented by thermograms in Figure 7. The exothermic maximum at 950 C is due to formation of CF and is independent of the relative proportions of CaO and Fe_2O_3. Melting effect is shown by an endothermic effect at 1150 C and is lower than the eutectic temperature of 1200 C in the phase diagram. The compound C_2F is formed subsequently, the minimum at 1300 C corresponding to an incongruent melting of the mixture.

The reactions in the ternary mixture containing CaO, Fe_2O_3 and Al_2O_3 are shown in Figure 8. An exothermic effect occurs at about 980 C owing to the formation of C_4AF. At lower contents of Al_2O_3, C_2F is also formed, indicated by an endothermic dip at about 1160 C.

The effect of various mineralizers, present in the mass or in the oven atmosphere, on the reaction products in cement manufacture has also been studied by DTA by Barta and co-workers.

HYDRATION REACTIONS

Hydration of Individual Phases in Cement Clinker

A study of the hydration of the individual components of the clinker compounds provides a better understanding of the complex reactions taking place in the cement. C_3S reacts quickly with water, producing $Ca(OH)_2$ and an ill-crystallized compound with C/S ratio of 1.5 to 1.8. The compound is nearly related to natural tobermorite, $C_5S_6H_5$, and is designated tobermorite gel.

Midgley studied the hydration product obtained by curing C_3S in water for 2 yr in the paste form (30). Thermograms indicated the presence of $Ca(OH)_2$, $CaCO_3$ and calcium silicate hydrate with the formula $1.77 CaO \cdot SiO_2 \cdot 3 H_2O$ ($CaO/SiO_2 = 1.77$) representing a poorly crystalline tobermorite, CSH(II). The gel gave a characteristic endothermic peak at about 120 C. Gaze and Robertson (31) studied by DTA the calcium silicate hydrate in commercial products. The exothermic reaction between 800 and 850 C was attributed to the transformation of CSH(I) to β-wollastonite. An endothermic peak at 760 C represented the presence of $CaCO_3$. Van Bemst (32) also studied the DTA of hydrates obtained by hydration of di- and tricalcium silicates. β-C_2S reacts at a slower rate and forms compounds similar to those resulting from C_3S. C_3A reacts very rapidly to form C_3AH_6, but its formation in cement is much debated. The DTA results of Kalousek et al (5) did not indicate the presence of C_3AH_6 in most of the cement pastes.

The DTA of C_3A after treatment with water shows a prominent bulge at 315 to 330 C (5, 105). Young (33) and Jones (64), however, found two endothermic effects corresponding to the stepwise dehydration of C_3AH_6. Gohlert (106) reported three peaks for C_3A pastes after 3 and 28 days of hydration. Budnikov et al. (107) and Sauman (108) also obtained three peaks. Govorov (109), however, reported four peaks. The differences in behavior of the hydrated C_3A reported by different workers could be attributed to the degree of purity of the sample, the temperature and quantity of water used, and the period of hydration. The sensitivity of the DTA apparatus is another factor which might have caused the nonregistration of minute effects.

The hydration reactions in the ferrite phase, C_4AF, proceed at a slower rate, contrary to earlier belief, and are much more complicated. Jones (34) has suggested that the ferrite phase forms a solid solution of $C_4A(aq)$-$C_4F(aq)$ as a first step in the transformation to $C_3A(aq)$-$C_3F(aq)$ solid solution.

Kalousek and Adams (35) followed the hydration of C_4AF by DTA. Thermal curves for hydrates of C_4AF with and without addition of gypsum are shown in Figure 9. The 7-day samples without gypsum showed the presence of the hydrogarnets and a small amount of hexagonal plates of $C_4A \cdot 13\,H_2O$. With increasing age, hydrogarnets decreased and $C_4A \cdot 13\,H_2O$ or a related phase increased, with a peak temperature at about 250 C. Hydrogarnets were represented by an endothermic effect at 300 to 400 C.

In cements, C_3A reacts with the retarder, gypsum, to form sulfoaluminates of compositions, $C_3A \cdot 3\,CaSO_4 \cdot 32\,H_2O$ or $3\,C_3A \cdot CaSO_4 \cdot 12\,H_2O$. It is not established which forms first in cement. In cements the formation of analogous sulfoferrites is also reported.

Hydration of Cement

DTA is considered one of the most powerful tools in the investigation of the hydration of cement pastes. Thermograms have yielded useful results on the cement hydrated for various lengths of time under different conditions (5, 30, 36, 37, 38, 39). Typical thermograms of portland cement hydrated for various periods as obtained by Greene (36) are shown in Figure 10. The unhydrated cement exhibits two endothermic peaks at 140 and 170 C due to stepwise dehydration of gypsum. The endothermal dent below 500 C is attributed to $Ca(OH)_2$ formed during exposure to air. The broad endothermic effect in the range 700 to 800 C is caused by the decomposition of $CaCO_3$, also formed by exposure to air. Five

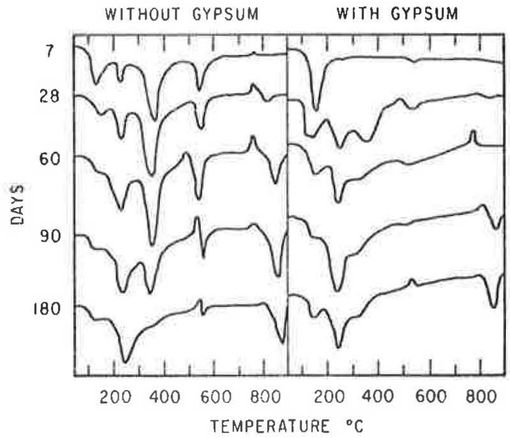

Figure 9. Thermal curves of C_4AF without and with gypsum and hydrated for various periods of time.

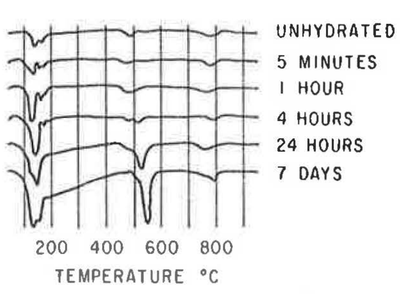

Figure 10. Thermograms of portland cement hydrated for various lengths of time.

minutes after hydration, an endothermic peak appears at 130 C due to the formation of high-sulfate calcium sulfoaluminate, $3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 31\,H_2O$. The decrease in gypsum content is evident from the reduction of the gypsum peaks. An hour after hydration, the intensities of the gypsum peaks decrease further and the peak due to sulfoaluminate becomes more pronounced. At 4 hr, an additional endothermic peak above 500 C is observed. The peak below 500 C is believed to be due to chemisorbed water on the surface of free lime particles, and that above 500 C to the more coarsely crystalline $Ca(OH)_2$ formed by crystallization through solution. After 24 hr of hydration, the double peak due to gypsum disappears and a small endothermic shoulder appears on the low temperature flank of the sulfoaluminate peak due to calcium silicate hydrate. After 7 days this endothermic peak increases. The appearance of a small endothermic peak at 200 C may be due to either the low-sulfate calcium sulfoaluminate, $3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O$, or to a solid solution of this compound with tetracalcium aluminate hy-

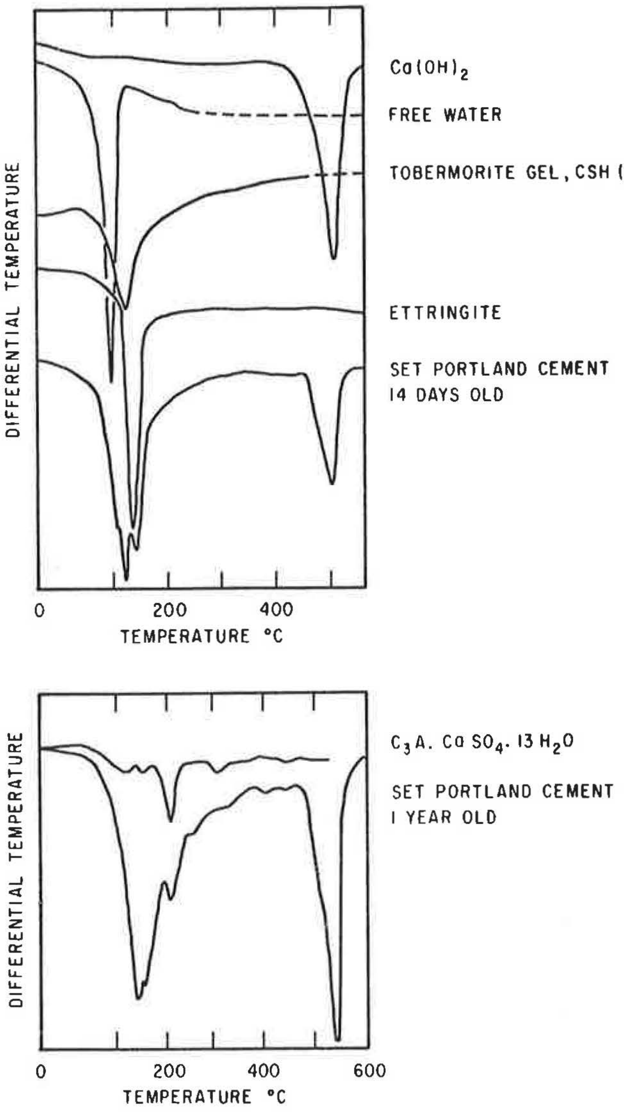

Figure 11. DTA curves of set portland cement and constituents.

drate, $4CaO \cdot Al_2O_3 \cdot 13H_2O$. The other important feature of the 24-hr and 7-day curves is the gradual loss of water in the range 200 to 500 C and increase in $Ca(OH)_2$ and $CaCO_3$ contents.

The thermal effects below 200 C in hydrated cements are of great interest in the interpretation of various reactions. Midgley (30) has discussed the endothermic peak effects obtained in a 14-day and 1-yr set cement. The three endothermic effects occurring very close to one another could be identified by comparing the standard thermograms of purer systems, such as $Ca(OH)_2$, free water, tobermorite gel CSH(II), ettringite and low sulfoaluminate (Fig. 11). The 14-day hydrated compound gives three peaks at 114, 127 and 147 C due to free water, CSH gel and ettringite, respectively. The set cement after 1 yr shows two endothermic peaks below 200 C and a peak above 200 C. The peak above 200 C corresponds to one of the peaks of the low sulfoaluminate. A quantitative estimation of tobermorite, ettringite and $Ca(OH)_2$ contents was attempted by Midgley by calibrating the peak area with different amounts of the purer substances. The estimation of $Ca(OH)_2$ content is relatively accurate. The figures given for tobermorite and ettringite are open to question, however, because there is no way of separating the individual peaks from the triple peak effect in the range 100 to 200 C.

There is some controversy regarding the type of sulfoaluminate that forms initially in cements, although it is widely held that the high sulfoaluminate forms first. Figure 12 obtained by Greene gives the DTA curves of cement clinker hydrated for various periods of time without the addition of gypsum. At 5 min, the curve shows a peak at 200 C due to either $4CaO \cdot Al_2O_3 \cdot 13H_2O$ or a related solid solution. The curve does not exhibit a low-temperature endothermic peak at 130 C, indicating that pure clinker compounds by themselves are not responsible for the peak. Addition of 2 percent gypsum produces a fairly large amount of high-sulfate form and prevents the formation of $4CaO \cdot Al_2O_3 \cdot 13H_2O$, indicated by the absence of a 200 C peak. The results do not seem to be conclusive and much more systematic work is needed to establish the products in the initial stages of hydration. For example, the endothermic peak at 200 C for sample containing 1 percent gypsum may be partly due to the presence of low-sulfoaluminate form which may convert to high form at higher gypsum concentrations. The low sulfoaluminate is reported to be the preferred product in presence of $Ca(OH)_2$ and $CaSO_4$ (40). The DTA work of Greene, in which the cement was hydrated for 2 min in distilled water as well as in saturated $Ca(OH)_2$-$CaSO_4$ solutions, showed only the endothermic peak corresponding to high-sulfoaluminate form in distilled water and the absence of any sulfoaluminate in $Ca(OH)_2$-$CaSO_4$. Turriziani and Schippa (41, 42) believed that DTA can be used to estimate semiquantitatively the sulfoaluminate phases in cement.

In the DTA of hydrated cement, a single peak at about 130 C is attributed to the high form of calcium sulfoaluminate hydrate, whereas the peak at about 200 C is attributed to the low-sulfate form. The DTA of purer sulfoaluminate, however, shows three peaks. The thermograms of the high- and low-sulfate forms obtained by Nemecek and Barta (110) are shown in Figure 13. The higher form containing 31 molecules of H_2O loses 21 molecules (zeolitically held) at 180 C, 3 molecules at 280 C, and the rest at 370 C. The monosulfate containing 12 molecules of H_2O loses 8 molecules (zeolitically held) at 160 C, 2 molecules at 230 C, and the most strongly held at 300 C.

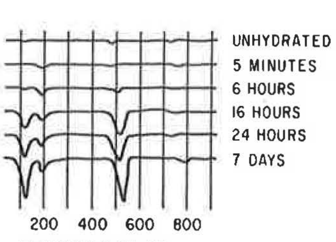

Figure 12. DTA curves of portland cement hydrated without gypsum.

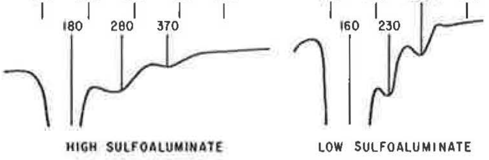

Figure 13. DTA of high and low calcium sulfoaluminate hydrates.

Figure 12 shows no indication of formation of the hexahydrate of C_3A in cement hydrated without gypsum. Kalousek et al. (5), however, reported the evidence of formation of C_3AH_6 in some clinkers by an endothermic effect at about 315 to 330 C. The other clinkers treated with gypsum did not exhibit the endothermic peak at 315 to 330 C. Only small amounts of SO_4 ions were required to suppress the formation of the hexahydrate.

Kalousek et al. believe that a solid solution is formed between $3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4$ (aq) and $3\,CaO \cdot Al_2O_3 \cdot 3\,Ca(OH)_2$ (aq) and also between the low sulfoaluminate $3\,CaO \cdot Al_2O_3 \cdot CaSO_4$ (aq) and $3\,CaO \cdot Al_2O_3 \cdot Ca(OH)_2$ (aq). Midgley and Rosaman (43) carried out DTA of three cements and found the first phase was pure calcium sulfoaluminate, with the solid solution containing calcium hydroxy aluminate hydrate after longer periods. Thermograms of the likely complexes of C_3A and C_3F are shown in Figure 14.

The role of ferrite phases in cement has been a subject of much controversy and is much more obscure. Malquori and Cirilli (44) and Schippa (45) presented evidence to show that calcium sulfoferrites analogous to high sulfate and low sulfate are formed. Watanabe and Iwai (46), by using x-ray and DTA, observed no compound corresponding to the composition $3\,CaO \cdot Fe_2O_3 \cdot 3\,CaSO_4 \cdot 31\,H_2O$ in the hydration of C_2F-$CaSO_4$. Budnikov and Gorshkov (47) discussed the relative stabilities of calcium hydro sulfoaluminate and calcium hydro sulfoferrite by DTA. Kalousek et al. (5, 35) carried out DTA to ascertain whether C_4AF produced hydrogarnet or a related hexagonal crystalline compound. The 7-day sample without gypsum (Fig. 9) shows an endothermic peak at about 350 C, indicating the presence of hydrogarnet, and one at 220 C, indicating the presence of a small amount of $4\,CaO \cdot Al_2O_3 \cdot 13\,H_2O$. At longer periods of hydration, hydrogarnet decreases and C_4AH_{13} or a related phase increases. The reaction is modified by gypsum. The 7-day sample after treatment with gypsum is essentially the sulfoaluminate and sulfoferrite of calcium. At 90 days, the product has a maximum of solid solution of $C_3A \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O$-$3\,CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12\,H_2O$ and, presumably, $3\,CaO \cdot Fe_2O_3 \cdot CaSO_4 \cdot 12\,H_2O$-$3\,CaO \cdot Fe_2O_3 \cdot Ca(OH)_2 \cdot 12\,H_2O$. In presence of gypsum, the hydration of $4\,CaO \cdot Al_2O_3 \cdot Fe_2O_3$ proceeds rapidly without the formation of hydrogarnets. Attempts were made to follow the effect of $Ca(OH)_2$ and gypsum on the hydration of $C_2F + C_4AF$. Several endothermic effects were observed, and the interpretation of the effects was incomplete (5).

The effect of humid air on the products obtained during the storage of cements has been followed by DTA (48). Water combines first with $CaSO_4$ and then with CaO and calcium silicate. The exothermic peak at 600 to 700 C found in the thermograms of cements was traced to the presence of sulfides.

Systems Containing CaO, SiO_2, Al_2O_3, Fe_2O_3, Etc., in H_2O

Studies on systems containing CaO, SiO_2, Al_2O_3, Fe_2O_3, alkalies and $CaSO_4$ in H_2O are of great importance in the chemistry and morphology of hydrous calcium-complex compounds. Kalousek (49-53) did extensive work on the CaO-SiO_2-H_2O system. The systems containing CaO-SiO_2-H_2O and CaO-Al_2O_3-H_2O were studied at room temperature by Kalousek et al. (5) and Jambor (54). The lime-silica gels show irregular exothermal bulges starting from 350 to 400 C and extending up to 500 C and an exothermic bulge at 800 to 890 C. Substitution of Al_2O_3 for silica

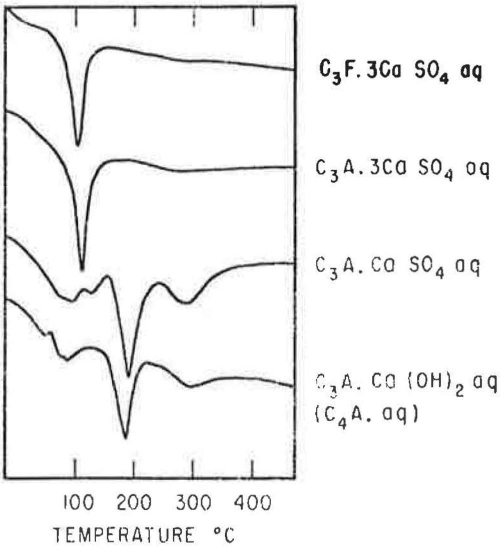

Figure 14. Thermograms of C_3A and C_3A-complexes.

gels shows, at 7, 14, and 28 days of aging, an endothermic bulge at 200 to 210 C and 470 C. The bulge at 200 to 210 C indicates the presence of $3CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12H_2O$. Newman (55) examined 15 mixtures containing $Ca(OH)_2$-SiO_2-H_2O in different molar ratios by DTA. Samples with different $Ca(OH)_2/SiO_2$ ratios and storage times and temperatures show characteristic thermal behavior. Some samples showed the presence of $C_3S_2H_2$. The behaviors of hydrous calcium silicates formed in the system CaO-SiO_2-H_2O with various C/S ratios were studied by DTA (56, 57), x-ray and electron microscopy. Tobermorite exhibited an endothermic effect at 260 C. The phase with C/S of 0.8 to 1.33 showed exothermic peaks at 830 and 900 C, and those with C/S of 1.5 to 2.0 exhibited peaks at variable temperatures. The DTA in conjunction with x-ray could be applied to differentiate 0.8 to 1.33 and 1.5 to 2.0 C/S hydrates.

The reactions in the system $Ca(OH)_2$-quartz (or silica) between 125 and 175 C in the molar composition range, 0.8 CaO/SiO_2 to 1.25 CaO/SiO_2, were studied by DTA (58). X-rays failed to differentiate between different compositions, whereas thermograms exhibited characteristic peaks. Figure 15 represents the DTA of products made with CaO-SiO_2 with 0.8 C/S (S = quartz) and autoclaved at 175 C for different periods (58). The 1-hr product shows the presence of $Ca(OH)_2$ by an endothermic effect between 500 and 600 C. At 1.5 hr, about two-thirds of $Ca(OH)_2$ is consumed to form poorly crystallized α-type hydrate. At 3.5 hr, there is almost complete absence of $Ca(OH)_2$ with an appearance of α-hydrate of 1.75 C/S. At longer periods reaction occurs between the lime-rich phase and the residual quartz. The formula for the 1.75 C/S product is $C_7S_4H_n$. The various steps in the reaction could be given as follows on the basis of thermograms:

$$7C + 4S + aq \rightarrow C_7S_4H_n$$

$$C_5S_4H_n + S \rightarrow 5CSH_n$$

$$4CSH_n + S \rightarrow C_4S_5H_n$$

$C_4S_5H_n$ converts to tobermorite, indicated by the 8-hr curve. Products of $Ca(OH)_2$-silicic acid mixture also followed a similar sequence, but the reaction was comparatively faster.

Midgley and Chopra (59) studied the lime-rich part in the system CaO-SiO_2-H_2O. Thermograms were obtained for mixes containing CaO/SiO_2 = 2:1 and autoclaved at 150 C. The mixture autoclaved for 30 days indicated a thermal peak at 460 C for the presence of α-C_2S hydrate. After 14 days of autoclaving at 180 C, DTA again showed the presence of α-C_2S hydrate. At 90 days, the presence of α- and β-C_2S hydrate was indicated. The peak at about 500 C was attributed to α-hydrate and that at 550 C to the β-hydrate. The mixture with CaO/SiO_2 ratio of 1 formed crystallized tobermorite. In another series of experiments, the autoclaved product of CSH(I) and lime resulted in an initial formation of Flint's CSH(A) and C_2S-α hydrate. With the starting material as β-C_2S, the product was C_2S-γ hydrate. β-C_2S and lime gave C_2S α-hydrate. With C_3S as the starting material, the product was $C_3S \cdot 1\frac{1}{2}H_2O$. The representative thermograms of various hydrates formed in an autoclaved-treated system are given in Figure 16. Bozhenov et al. (60) studied by DTA the hydrothermal reactions at 8.25 and 100

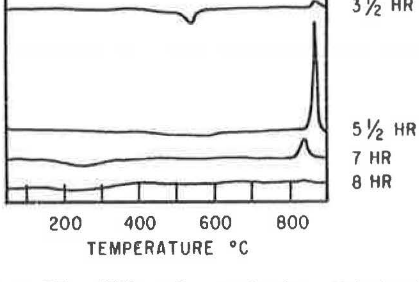

Figure 15. DTA of products obtained by autoclaving 0.8 C/S mixture at 175 C.

atm by adding various quantities of CaO and SiO_2 to β-C_2S. Lime-sand autoclaved products showed many endothermic effects. The effect in the range 120 to 400 C was due to dehydration of zeolitic water from the gel structural component, at 450 C it was due to $Mg(OH)_2$ decomposition, at 573 C to the $\alpha \rightarrow \beta$ conversion in quartz, at 680 to 750 C it corresponded to the dehydration of crystalline calcium hydrosilicate. Recrystallization of dehydrated silicates was manifested by a sharp exothermic reaction in the range 800 to 850 C. Further information on CaO-SiO_2-H_2O under hydrothermal conditions has been published recently (61).

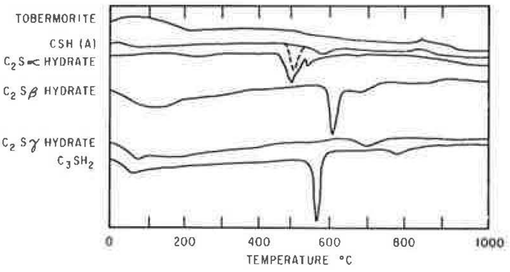

Figure 16. Differential thermograms of various calcium silicate hydrates.

The DTA of products formed by hydrothermal interaction of lime, with or without addition of cement, with siliceous aggregates such as silica, pumice, expanded shale or slag showed certain characteristic properties of the products (51, 62). Autoclaved products with cement-lime and silica (or quartz) consist of a series of hydrates having a composition from about 0.9 to 1.3 C/S. The mixes different in silica fines formed a poorly crystalline lime-rich phase. With pumice, cement-lime formed hydrates structurally similar to those made from quartz but with C/S ratio higher than 1.3. DTA successfully differentiated between phases of different compositions. The DTA was applied by Midgley and Chopra (63) to identify the compounds formed by hydrothermal reaction of lime with aggregates such as fuel ash, expanded colliery shale, ground quartz, granulated and foamed blast furnace slag. Tobermorite and a hydrogarnet were formed with pulverized fuel ash or shale as aggregates, tobermorite and zonotlite with quartz, poorly crystalline tobermorite, dicalcium silicate α-hydrate and a hydrogarnet with slag.

Attempts have been made to study the DTA of quaternary system, CaO-Al_2O_3-$CaSO_4$-H_2O (41). DTA shows the presence of new phases, $C_4A \cdot 13\,H_2O$ and $C_3A \cdot CaSO_4 \cdot 12\,H_2O$. Majumdar and Roy (64) used DTA to study the system CaO-Al_2O_3-H_2O between 100 and 1000 C under water pressures up to 3000 atm. DTA showed only endothermic peaks for the presence of $Ca(OH)_2$, C_3AH_6 and $C_4A_3H_3$.

Autoclaved Portland Cement Products

Setting and hardening of concrete products can be accelerated by curing them in steam at 180 C and at a pressure of 100 to 200 psi. In this type of curing, the cement is mixed with about 60 percent of its weight with fine quartz or other reactive silica and aggregate. Crystalline tobermorite is the main product formed by autoclave treatment. In absence of reactive silica, α-C_2S is the product responsible for low strengths. No free $Ca(OH)_2$ is detected. The reaction of C_3A and the ferrite phase is not well known.

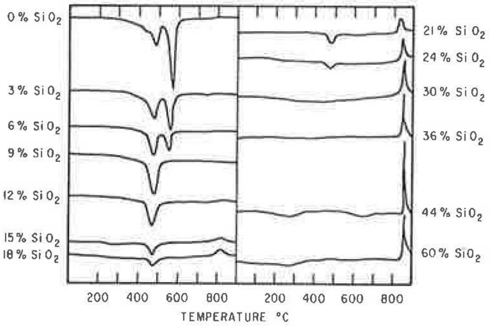

Figure 17. Thermal analysis of cement-silica mixtures processed at 175 C for 24 hr.

Kalousek and Adams (35) carried out a systematic investigation of the cement-silica (finely ground quartz) mixtures by autoclaving at 175 C. The DTA of the products containing SiO_2 up to 60 percent is given in Figure 17. The peak due to decomposition of $Ca(OH)_2$ at 560 C is observed only in the products containing less than 9 percent SiO_2. The absence of

$Ca(OH)_2$ decomposition peak is due to the reaction between SiO_2 and $Ca(OH)_2$. The endothermic effect at 470 to 480 C was identified as plate-like dicalcium silicate hydrate and was present in larger amounts up to 9 percent SiO_2, after which it decreased progressively. Menzel (65) had reported earlier that 8 to 10 percent SiO_2 product corresponded to minimum strength and at this composition, a maximum amount of plate-like dicalcium hydrate was observed. At higher SiO_2 concentrations, an exothermic peak appears at 840 C, with a maximum inflection at a composition of 40 to 45 percent SiO_2; this also corresponds to greatest strength. Hence, the high strength was ascribed to the phase responsible for the exothermic peak and was designated monocalcium hydrate. Subsequent studies showed that high strengths in the autoclaved products were due to the presence of tobermorite. The formation of α-C_2S always resulted in articles of poor strength. Bozhenov et al. (60, 66) presented results of DTA on autoclaved cement pastes obtained at 8 to 100 atm. Thermograms of products formed from C_2S in admixture with CaO and SiO_2 were examined. Evidence was found for an interaction between β-C_2S and SiO_2 with the formation of basic calcium hydrosilicates (67). DTA was applied by Kalousek (51) to examine the autoclaved products obtained with different raw materials made of lime-cement and aggregates such as silica, pumice, expanded shale or expanded slag. The salient results obtained by him have already been discussed.

EFFECT OF EXTRANEOUS COMPOUNDS ON CEMENT HYDRATION

Reactions of $CaCO_3$ and CO_2 With Cement

The possibility of formation of complex compounds such as carboaluminates in cements in presence of CO_2, $CaCO_3$ or alkali carbonates has received some attention in recent years. Bessey (68) prepared the high- and low-carbonate forms, $3\,CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot xH_2O$ and $3\,CaO \cdot Al_2O_3 \cdot 3\,CaCO_3 \cdot xH_2O$. Turriziani and Schippa (69) identified the low-carbonate form in alumina cement pastes cured for 2 yr. Carlson and Berman (70) obtained a product of the probable formula, $3\,CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11\,H_2O$, in mixtures of CaO-Al_2O_3-H_2O exposed to CO_2. Greene (36) found a difference in the thermograms of cement hydrated with water and that hydrated with 2 percent Na_2CO_3 for 24 hr. The difference was attributed to the formation of carboaluminate. These thermograms for carboaluminates are shown in Figure 18 for comparison. Although these may represent the carboaluminates, it is rather difficult to believe they are identical. No attempt has been made by any of these workers to discuss various peaks, and much more systematic work seems to be needed to establish definitely the thermal behavior of carboaluminates.

Manabe et al. (71) carried out TGA of the system C_3A-$CaCO_3$-H_2O and reported the formation of $3\,CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10.6\,H_2O$. The carboaluminate was formed after 3 days in a mixture of cement and $CaCO_3$.

Cole and Kroone (72) carried out DTA to investigate how CO_2 reacted with portland cement mortar and calcium silicate hydrate. Contrary to earlier views that only calcite is formed, poorly crystallized vaterite and aragonite in addition to some calcite were found.

The possibility of the occurrence of calcium silicoaluminates analogous to sulfoaluminates has been reported by Flint and Wells (73). The compound $3\,CaO \cdot Al_2O_3 \cdot 3\,CaSiO_3 \cdot 30\text{-}32\,H_2O$ reported by Flint was re-examined by DTA by Carlson and Berman (70). The compound which had been exposed to CO_2 indicated an endothermic effect for the expulsion of water at the same temperature found for $3\,CaO \cdot Al_2O_3 \cdot 3\,CaCO_3 \cdot 32\,H_2O$. The endothermal peak found at 815 C was due to CO_2 evolution. The exothermic effect at 850 C was due to lime-silica reaction. The significance of other irregularities in the thermal curves was not discussed. The conclusion, however, was that the silicoaluminate in presence of CO_2 forms a mixture of aluminate silicate and carboaluminate.

Work on the effect of various amounts of $CaCO_3$ on the hydration of C_3A has been carried out at the Division of Building Research by the authors (results unpublished). The results of dimensional changes in the compacts formed from C_3A and C_3A-$CaCO_3$ and hydrated in water were correlated with those obtained by DTA. Thermograms showed that hydrated C_3A exhibits an intense endothermal effect with a peak at 310 C and additions of $CaCO_3$ suppress this peak. A carboaluminate complex formed on the surface of the C_3A grains also appeared to inhibit further hydration.

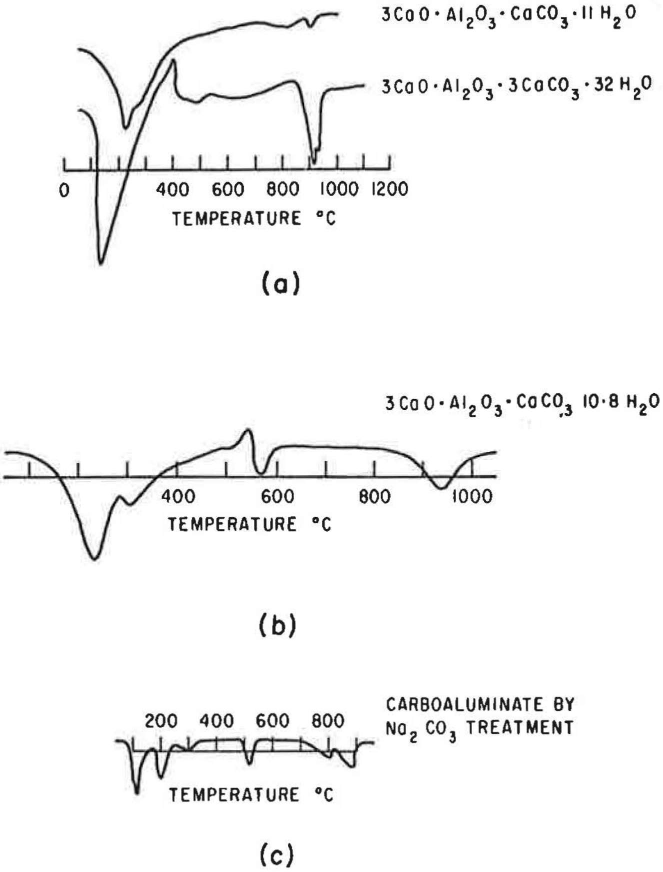

Figure 18. DTA of carboaluminates: (a) Carlson and Berman; (b) Turriziani and Schippa; and (c) Greene.

Surface Active Agents

Addition of small quantities of salts of lignosulfonic acid to concrete lowers the water requirement and retards the setting of the concrete mix. DTA was applied by Young (33) to study the role of lignosulfonate on the hydration behavior of C_3A alone and in presence of gypsum and lime. No attempts were made to explain some of the thermal peaks. It was concluded that in pastes of C_3A, lignosulfonates favor the formation of C_2AH_8 and C_4AH_{13} and modify their crystal habit. In presence of gypsum and lime, formation of low sulfoaluminate form is favored. In Figure 19 are represented the DTA of the typical mixtures obtained by Young. The C_3A hydrated product shows two endothermic peaks; the one at 300 to 400 C was also reported by others as being due to C_3AH_6. In presence of lignosulfonate, three endothermic peaks are obtained below 400 C and are attributed to a mixture of C_4AH_{13} and C_2AH_8. The exothermic peak at 520 C was not satisfactorily explained. C_3A paste with gypsum and lime shows endothermal effects at 100, 210, 320, 520 and 820 C. These are due to low-sulfoaluminate form, C_2AH_8 and C_4AH_{13}. The same mixture in presence of lignosulfonate gave less intense endothermal effects due to retardation of the hydration reaction.

False Set

Some cements exhibit the phenomenon of "false set" or premature stiffening. Various theories of false set have been reviewed by Blanks and Gilliland (74). According

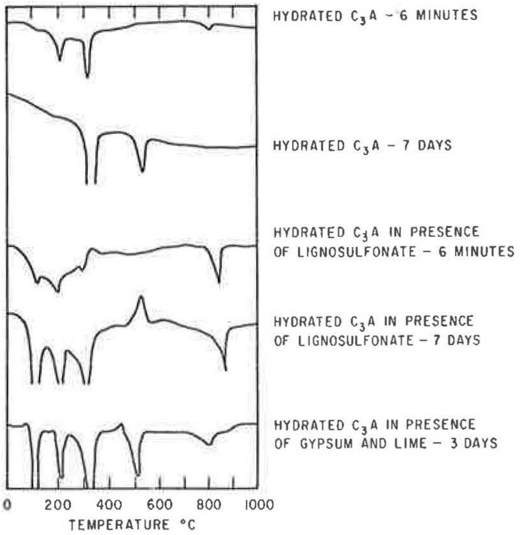

Figure 19. DTA of C_3A hydrated in presence of lignosulfonate and gypsum and lime.

to general views, false set is due to dehydrated gypsum in the form of hemihydrate or soluble anhydrite or both, rapidly precipitating as gypsum without the evolution of much heat.

Takemoto et al. (75) studied by DTA the extent to which gypsum had dehydrated during grinding of a mixture of clinker and gypsum in an experimental mill. The DTA curves showed that the hemihydrate was formed at 85 C when ground for 40 min. The soluble anhydrite was formed at 130 C when the grinding time was 80 min. Gilliland (76) studied the DTA behaviors of gypsum, hemihydrate, insoluble anhydrite, and a cement as received and when heated to 300 C. Gypsum showed two endothermic peaks at 190 and 210 C due to loss of 1½ molecules and ½ molecule of water, respectively. The exothermic peak at 380 C initiated the conversion of soluble to insoluble anhydrite. The hemihydrate exhibited an intense endothermic peak above 200 C owing to the loss of ½ molecule of water. No thermal effect was observed for $CaSO_4$ (insoluble). A commercially ground cement showed two peaks at 140 and 160 C; that the latter was larger was attributed to the formation of hemihydrate from the gypsum present in the cement. The soluble anhydrite was formed by heating the cement at 300 C and then cooling. Soluble anhydrite partially converted to hemihydrate on exposure to air, showing a peak at 130 to 135 C. Fischer (111) evaluated quantitatively the degree of dehydration of gypsum in cement by DTA.

OTHER CEMENTS

Alumina Cement

The special type of cement known as "aluminous cement," characterized by a high early strength is formed by firing limestone or chalk with bauxite to a temperature of 1550 to 1600 C.

Alumina cement contains compounds such as unstable C_5A_3, CA and C_2AS. CA, the most important constituent, reacts with water at room temperature to form CAH_{10}, the principal cementing agent. Under hot humid conditions, CAH_{10} transforms to C_3AH_6 with a loss in strength. Pole and Moore (77) and Schneider (112) obtained DTA of alumina cement paste. The endothermic effect between 250 and 350 C showed the presence of C_3AH_6. An exothermic peak extending over a wide range of 400 to 1000 C was perhaps due to the burning of carbon present in the cement slag. Nagai and Harada (78, 79) studied three alumina cements, CA and C_3A_5 by DTA. Rey (38) showed by DTA that the aluminous cement hydrated for 7 days exhibits peaks corresponding to tetracalcium aluminate hydrate and at 13 days to dicalcium aluminate hydrate. The various inflections in the thermograms were not accounted for.

Pozzolanas and Pozzolanic Cements

Pozzolanas are materials which combine with lime at ordinary temperatures in presence of water to form stable insoluble compounds possessing cementing properties. Pozzolanic cements are obtained by grinding together portland cement clinker and pozzolana or mixing together a hydrated lime and a pozzolana (80). There is every reason to believe that pozzolanic materials form cementitious compounds similar to those obtained by the hydration of portland cement clinker.

Turriziani (81, 82) has applied the DTA technique extensively to a study of the chemistry of the pozzolanic activity. He reported that a pozzolana treated with saturated lime solution gave a low temperature endothermic peak at 140 C, indicating the presence of Taylor's silicate, CSH(I). The second effect at 200 C was ascribed to the presence of C_4AH_{13}. Continued work (83) on the products with different proportions of $Ca(OH)_2$ and pozzolana and on mortars confirmed the presence of calcium silicate of tobermorite type. In mortars, DTA showed the presence of C_4AH_{13}. The reaction at 45 C gave the product with a peak corresponding to C_3AH_6 (cubic). This agrees with results obtained by Malquori and Cirilli (84). The formation of small amounts of C_2SAH_X was also considered. The determination of free $Ca(OH)_2$ in pozzolanic cements by DTA showed that after long curing the quantity is much smaller than that ordinarily formed in portland cement pastes (85). The products of portland cement-pozzolanas examined up to a period of 1 yr showed the presence of tobermorite type of calcium silicate hydrate, tetracalcium aluminate hydrate, high-sulfate sulfoaluminate and low $Ca(OH)_2$ content. A mixture of pozzolana, hydrated lime and gypsum in water shows an endothermal peak corresponding to the formation of $3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32\,H_2O$ and under certain conditions, $3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O$ (86, 87). Rey (38) also presented a typical curve for $Ca(OH)_2$-pozzolana mixture. Surovkin and Krylov (88) studied the interaction of lime and calcined clay. DTA showed exothermic peaks at 310 and 890 C and an endothermic peak at 540 C for the reaction between calcined clay and $Ca(OH)_2$. Benton (113) carried out a systematic investigation of the lime-pozzolan and cement-pozzolan reactions by DTA and x-ray. The pozzolans used for the study included pumicite, diatomite, kaolinite, bentonite, illite, gibbsite, quartz and fly ash. The DTA of all lime-pozzolan mixtures except quartz showed endothermic peaks at about 200 C for the presence of C_4AH_{13}. All mixtures exhibited endothermic peaks between 500 and 600 C, corresponding to $Ca(OH)_2$ decomposition, and the intensity of the peak was used to determine the reactivity of the pozzolans in lime-pozzolan and pozzolan-cement mixtures. In cement-pozzolan mixtures, high-temperature exothermic peaks increased in intensity for more active cements; this was correlated with dehydration of products into such minerals as wollastonite, β-C_2S and melilite. A much more systematic work should be undertaken to study the interaction between clay minerals fired to different temperatures and treated with limes of varying reactivity.

Slag Cements

Slag cements are obtained by grinding granulated blast furnace slag (by quenching the slag issuing from the blast furnace at 1400 to 1500 C) with activators such as portland cement clinker or hydrated lime and a mixture of one or other of these with gypsum or anhydrite.

The chemistry of slag cements is less clear than that of portland cement. Lommatzsch (89) tried to obtain an understanding of binding and setting processes of granulated blast furnace slags under sulfate activation. The thermal changes in the range 800 to 900 C were thought to be due to modifications and formations typical of the hydraulic basic slags. The formation of glass in the slag was studied by Kondo (90). Williams and Chopra (91) found that Indian slags containing 25 percent $CaSO_4$ and 5 percent cement clinker formed a good-quality supersulfated cement. The DTA of this mix indicated the presence of ettringite at curing periods extending from 3 to 90 days. The intensity of the endothermic effect at 160 C gave an indication of the amount of ettringite formed. DTA has been applied by some workers to characterize the blast furnace slags (92, 93). Mchedlov-Petrosyan et al. (94) recently found that DTA is a rapid test method for the detection of glass in slags.

The mechanism of activation of slags was studied by Samaddar and Lahiri (114). Synthetic slags with a constant SiO_2/Al_2O_3 ratio and varying CaO contents were prepared with lime-gypsum mixture. DTA results showed the presence of C_4AH_{13} as an initial product on the surface. During hydration the hydrate liberates lime which reacts further with mass of the slag.

CONCLUSIONS

The introduction of DTA technique into the field of cement chemistry is only recent and it is certain that the method would play a role especially in the investigation of materials not easily discernible by x-ray diffraction.

The thermographic characteristics of similar materials reported by different workers vary considerably. Hence, factors such as heating rate, particle size, weight of the sample, furnace atmosphere, type of the specimen block, purity of the material (where possible), and method of drying must be specified.

The low-temperature endothermic peaks in cements provide a basis for the identification of the starting material. The method of drying is very critical in hydrating cements and, without proper precautions, may interfere with the low-temperature effects.

The identification of any material in cement in terms of peak temperatures presents difficulties because of the shift in the peak temperature caused by the presence of other materials. It would be helpful to calibrate the peak temperatures by running a DTA of mixtures of known amount of materials present or formed during a treatment.

For substances exhibiting small energy changes over a wide temperature range, the rate of heating should not be high so as to outstrip the rate of attainment of equilibrium. Spurious results, such as the development of two depressions in place of one, are not uncommon.

DTA, as any other technique, has certain limitations and the results should be interpreted cautiously and preferably in conjunction with other techniques. DTA could advantageously be used for quantitative work. Many attempts have been made to increase the sensitivity of the method so that it could be used as a quantitative tool (95-98, 115-120).

Another field of study in which DTA offers promise is in the investigation of the nature of water alone and in presence of salts in porous systems at fairly low temperatures.

The progress in the DTA of cement chemistry may be compared to the parrallel development in its application in clay mineralogy. It is reasonable to expect that the application of this technique in cement chemistry will greatly increase. In the field of clay mineralogy, with the introduction of DTA, there was a tendency among clay workers to apply the method rather indiscriminately without regard to precautions and limitations. Consequently, thermograms reported for a particular mineral by one laboratory differed greatly from that reported by the other. It was in this context that an International Geological Congress was held in London in 1948 to recommend certain specifications for the standardization of the technique. It is perhaps pertinent to indicate in this connection that DTA will probably continue to enjoy popularity in cement chemistry and it is advisable at this stage to formulate certain standards to aid workers in the interpretation and comparison of results.

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Studies on Tobermorite-Like Calcium Silicate Hydrates

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Parallel studies were carried out on certain characteristics of CSH(I) synthesized at room temperature and on tobermorite gel produced by paste or bottle hydration of β-C_2S, C_3S, and alite. Instrumental methods employed included x-ray diffraction, DTA, infrared spectroscopy, and electron microscopy. Surface areas of the CSH(I) samples were measured by water vapor adsorption, and heats of adsorption were calculated. Both CSH(I) and tobermorite gel had negative surface charge in the absence of $Ca(OH)_2$. A method was devised to measure the cation exchange capacities of these materials, which were on the order of 5 to 25 meq/100 gm.

CSH(I) appears to be a distinct and reasonably homogeneous physicochemical entity despite compositional variation, and similarly the tobermorite gel products appear to be members of a distinct phase regardless of the particular cement mineral or mode of hydration used. The two phases exhibited similar surface properties, and the primary particles of both seemed to be intrinsically cemented into microaggregates. The two phases are difficult to differentiate by x-ray methods but may be distinguished from each other by particle morphology, by the intensity of the high-temperature exotherm on DTA, and to some extent, by their infrared spectra.

•THE poorly crystallized calcium silicate hydrates (CSH) that resemble the well-crystallized mineral tobermorite comprise a group of materials of importance to cement chemists, and are also of theoretical interest. The present work is an attempt to characterize in detail some of the properties of two of these phases, CSH(I) and tobermorite gel. The latter has also been known as "CSH (gel)" and "tobermorite (G)." The approach employed features the study of a number of relevant properties of a suite of what is hoped are representative materials of each kind, prepared in several different ways. Methods of study include x-ray diffraction, DTA, electron microscopy, infrared spectroscopy and water-vapor adsorption. Somewhat parallel studies were carried out with certain synthetic well-crystallized tobermorites, primarily to determine the effects of lattice substitution; these will be reported elsewhere.

Reference to much of the published work in this field is made difficult by the conflicting terminology used in designating the individual phases, and by failure of some workers consistently to distinguish between tobermorite itself and the several poorly crystallized phases now recognized. Reviews by Taylor (1) and by Brunauer and Greenberg (2) contain considerable information on the known properties of these materials.

CSH(I) is a poorly crystallized synthetic CSH distinct from, but related to, tobermorite. It can be prepared by reaction at room temperature or under hydrothermal conditions (3). The structure is a layer structure related to that of tobermorite, but details are not known with certainty. X-ray diffraction patterns display peaks at the

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positions of the strong (hkO) lines of tobermorite; a diffuse basal spacing is sometimes observed in the approximate range of 10 A to 14 A, depending on the state of hydration and the Ca:Si ratio of the particular material (1). CSH(I) specimens showing similar x-ray patterns have been prepared in which the Ca:Si ratio may vary from 0.8 to approximately 1.5. The DTA pattern of CSH(I) is characterized by a strong, sharp high-temperature exothermic peak at 850 to 900 C (4). Electron microscopy reveals a particle morphology generally described as consisting of crinkled or crumpled foils; the foils are usually only a few unit layers in thickness (5, 6).

Tobermorite gel is produced by paste or bottle hydration of C_3S, or by paste or ball-mill hydration of β-C_2S, under room-temperature conditions. X-ray diffraction shows only three peaks, corresponding to the positions of the strongest (hkO) lines of tobermorite; basal spacings have not been observed, except in a single instance (2). The detailed structure is unknown, but it is thought to be related to that of tobermorite. This is a comparatively high-lime phase with Ca:Si ratio normally varying from about 1.4 to 1.7. Tobermorite gel is usually considered to consist of mostly straight, comparatively long fibers, the fibers themselves being composed of rolled sheets. An adequate DTA pattern for a pure tobermorite gel phase has not previously been published, although partial information is available (2).

Bottle hydration of β-C_2S is said to give rise to a distinct phase called CSH(II) (7), which may also be formed on extended reaction of C_3S in supersaturated lime solution (8), as an initial product in hydrothermal reaction (3) and, reportedly, by reaction of calcium glycerate solution with silica gel (9). CSH(II) is a lime-rich phase with Ca:Si ratio of 1.5 to 2.0; thus, its composition overlaps that of tobermorite gel. In contrast to the latter, an x-ray basal spacing of about 10 A is generally recorded (1). It has been suggested that this phase can be identified by an x-ray peak at 1.5 A (10). Again, the detailed structure is unknown. The morphology is fibrous, and cigar-shaped bundles of fibers of distinctive appearance are often observed (5, 7). The DTA pattern is marked by an exothermic bulge at about 400 to 450 C, and by a relatively small high-temperature peak in the 850 C region (4).

PREPARATION OF SAMPLES

CSH(I)

Seven samples of CSH(I) were prepared by several methods, all of which involved reactions at room temperature. Five were made by double decomposition reactions, and two by direct synthesis from lime and silica.

Four samples were prepared in the same general manner, in which solutions of sodium silicate and a calcium salt were poured simultaneously into a third container and vigorously stirred, the CSH precipitating as large white flocs. The sodium silicate used was 0.5 N in each instance; the calcium salt solution used was 0.5 N $CaCl_2$ in one sample, 0.5 N $Ca(NO_3)_2$ in the others. The Ca:Si molar ratios were 1.0 for the sample prepared with $CaCl_2$ and one of the samples made with $Ca(NO_3)_2$, and 1.5 and 2.0, respectively, for the other two samples made with $Ca(NO_3)_2$. After precipitation, the products were diluted with distilled water, filtered over suction, washed several times (first with water,. then with acetone, and finally with ether), and dried at 110 C.

A fifth sample was prepared by a more elaborate procedure, devised to promote microscopic homogeneity. Two 10-ml Luer-lock syringes were mounted obliquely to each other with their tips almost touching, so that when the syringes were simultaneously depressed the two fine streams produced were intimately mixed and the combined droplets produced fell into a flask mounted below the syringes. The contents of the flask were stirred continuously. Separate reservoirs were attached to the two syringes so that they could be repeatedly refilled without disturbing the arrangement. Two hundred ml each of solutions of sodium silicate and calcium nitrate were loaded into the respective reservoirs and mixed by simultaneously depressing the syringes, reloading, and repeating the process. The concentrations of the solutions were adjusted to yield a Ca:Si molar ratio of 3.5 to get a high-lime product. After all solutions had been reacted, the precipitated material was filtered and washed exhaustively, this time starting with saturated $Ca(OH)_2$ solution. The washing was continued using a

TABLE 1

DESIGNATION, ORIGIN, AND COMPOSITION OF CSH(I) PRODUCTS

Sample No.	Starting Materials	Ca:Si Ratio of Reactants	Composition of Final Product
CSH(I)-1	Na_2SiO_3, $CaCl_2$	1:1	$C_{0.97}S_{1.00}H_{2.74}$
CSH(I)-2	Na_2SiO_3, $Ca(NO_3)_2$	1:1	$C_{0.96}S_{1.00}H_{1.59}$
CSH(I)-3	Na_2SiO_3, $Ca(NO_3)_2$	1.5:1	$C_{0.99}S_{1.00}H_{1.62}$
CSH(I)-4	Na_2SiO_3, $Ca(NO_3)_2$	2:1	$C_{1.01}S_{1.00}H_{1.64}$
CSH(I)-5	Na_2SiO_3, $Ca(NO_3)_2$	3.5:1	$C_{1.16}S_{1.00}H_{1.00}$
CSH(I)-6	SiO_2, $Ca(OH)_2$	1:1	$C_{0.91}S_{1.00}H_{1.08}$
CSH(I)-7	SiO_2, $Ca(OH)_2$	2:1	$C_{1.58}S_{1.00}H_{1.80}$

water-acetone mixture, acetone, and finally ether, and then the washed sample was dried at 110 C under vacuum.

Two samples were prepared by direct reaction of a concentrated silica sol (Nalco-Ag 10-22, National Aluminate Co.) with reagent-grade $Ca(OH)_2$. The first preparation was made by direct addition of the reagents in 1:1 molar proportion. The resulting suspension was diluted with distilled water and transferred to a polyethylene bottle. This was rotated on a roller mill for 2 days, then allowed to stand undisturbed for 3 wk. The aged precipitate was then filtered, the initially cloudy filtrate being recycled until the effluent solution was clear. The pH of the filtrate was 10.6, suggesting that all free $Ca(OH)_2$ had reacted; consequently, the sample was washed once with water and dried. A second preparation was made in the same way except that a Ca:Si ratio of 2.0 was used; here the pH of the recycled and clarified filtrate was 12.5, indicating that unreacted $Ca(OH)_2$ was present. The product was washed with water until the pH dropped below 12.3 and x-ray examination disclosed the absence of crystalline $Ca(OH)_2$. After one additional wash the sample was dried and stored.

The samples are designated CSH(I)-1 through CSH(I)-7. Chemical analyses were carried out by standard methods and the conventional compositional formulas were determined (Table 1). Considering that the molar ratio of starting mixtures varied from 1.0 to 3.5, the fact that the observed Ca:Si ratios of the five samples made by double decomposition were all so close to 1 is somewhat unexpected. In contrast, the CSH(I)-7 sample, prepared by direct synthesis and aged prior to washing and drying, had a Ca:Si ratio of almost 1.6. Although this ratio is slightly higher than the upper limit normally ascribed to CSH(I), this sample appears to be CSH(I) rather than CSH(II).

Tobermorite Gel

Tobermorite gel samples were prepared by hydration of β-C_2S, C_3S and alite. Paste hydration of the β-C_2S and C_3S samples was carried out at 23 C using a water:solids ratio of 0.7, and the hydration was allowed to proceed for 7 mo. Bottle hydration at the same temperature was carried out in polyethylene bottles rotated on a wheel at approximately 30 rpm; the water:solids ratio was 9.0. Bottle hydration of the β-C_2S and C_3S samples was allowed to proceed for 6 mo, and of the alites for 4 mo. In all experiments freshly boiled distilled water cooled below room temperature was used, and the containers were sealed against carbon dioxide penetration.

The designations for the specific samples studied are given in Table 2. In addition to the samples listed, bottle hydration products for an additional sample of C_3S and of alite were prepared and examined, but the results were essentially identical to those discussed.

TABLE 2

DESIGNATION AND PREPARATION OF TOBERMORITE GEL PRODUCTS

Gel Designation	Starting Material	Source and Number	Hydration	
			Method	Time (mo)
P-1	β-C_2S	PCA B-91	Paste	7
P-2	C_3S	PCA B-101	Paste	7
B-1	β-C_2S	PCA B-91	Bottle	6
B-2	C_3S	PCA B-101	Bottle	6
B-3	Alite	PCA B-93	Bottle	4
B-4	Alite	Univ. Calif.	Bottle	4

CSH(II)

Several attempts were made to prepare CSH(II) by the synthesis described by Toropov et al. (9). CaO from freshly calcined $CaCO_3$ was mixed with silica gel, using a Ca:Si ratio of 2.0. The mixture was ground under several drops of glycerol, placed in a flask with the specified amount of hot, dried glycerol, and stirred continuously while being heated over a hot plate. Toropov et al. reported that their mixture began to froth at 180 to 185 C and continued for several hours until the liquid became clear. However, no such action occurred despite extended heating, and after several trials the attempted synthesis was abandoned.

X-RAY DIFFRACTION

The dried and powdered samples were examined by x-ray diffraction. A General Electric XRD-5A instrument employing nickel-filtered copper radiation was used. Samples were prepared as randomly oriented powder specimens by a slight modification of the method of McCreery (12).

X-ray diffractometer traces for all seven CSH(I) samples are shown in Figure 1. Five of the seven, CSH(I)-3 through CSH(I)-7 are remarkably alike. All have the strong main peak at around 3.05 A, which characterizes tobermorite-like CSH, and weak peaks at about 2.78 and 1.8 A. No peak occurs at or near 1.56 A, which would characterize the phase CSH(II), even for the high-lime sample CSH(I)-7. It is sometimes loosely

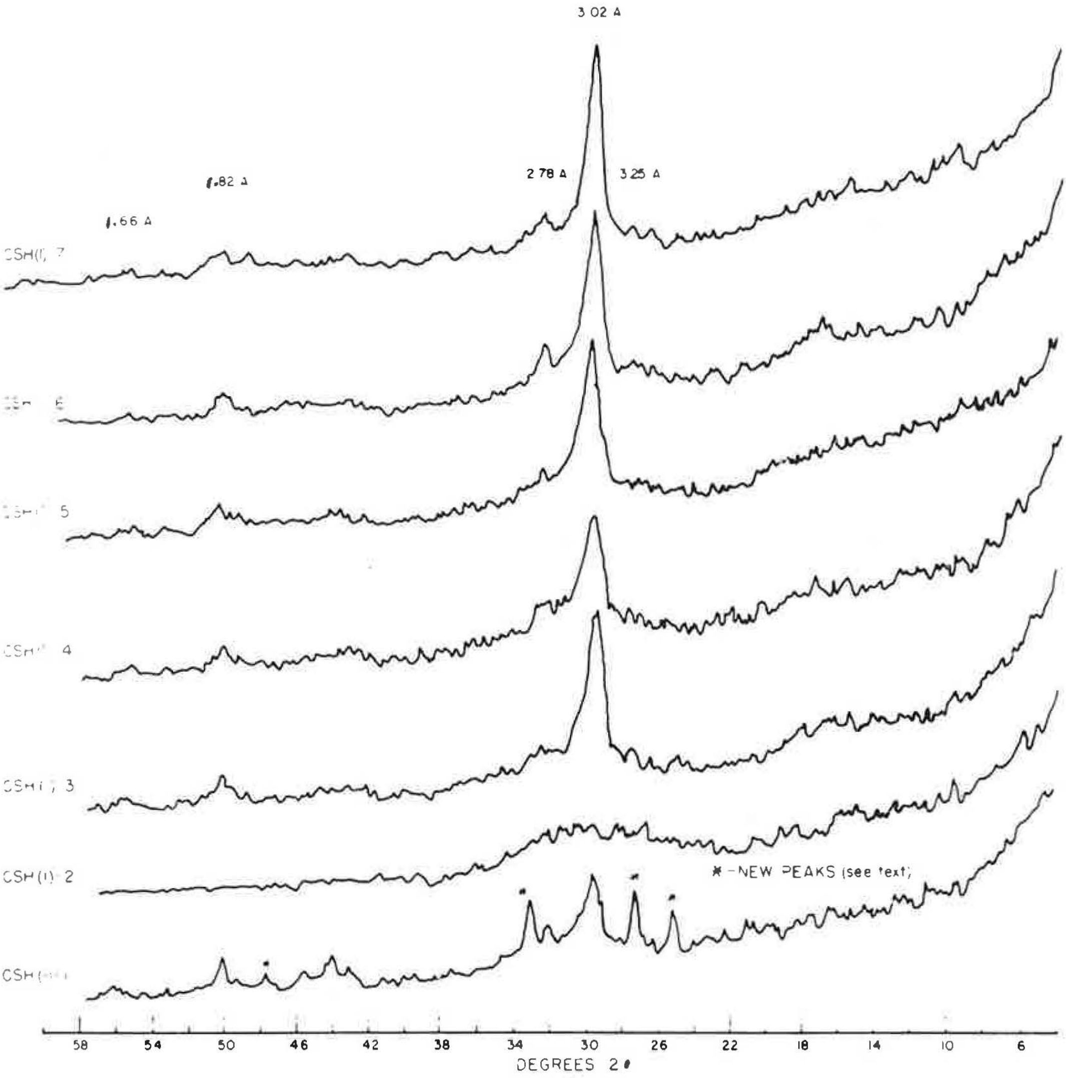


Figure 1. X-ray diffractometer traces for CSH(I) samples.

stated that CSH(I) exhibits the three strongest peaks of tobermorite. Well-crystallized tobermorite has a peak at 2.97 A, the (222) reflection, that is always greater in tobermorite than the 2.8 and 1.8 A peaks, but there is no evidence for the former peak in these patterns. Furthermore no basal peaks are observed. This suggests that the present material is disordered in the c-axis direction, the peaks available being all reflections from planes of atoms entirely within the unit layer.

One sample, CSH(I)-2, seems to be essentially amorphous to x-rays; however, the broad general diffraction in the 3 A region may indicate some short-range order.

The pattern for CSH(I)-2 displays peaks for vaterite (μ-$CaCO_3$). Originally, diffraction runs made shortly after preparation of this sample showed a pattern similar to the other weakly crystalline CSH(I) samples. However, re-examination after storage for approximately 1 yr produced the pattern shown in Figure 1, indicating that carbonation had taken place on storage.

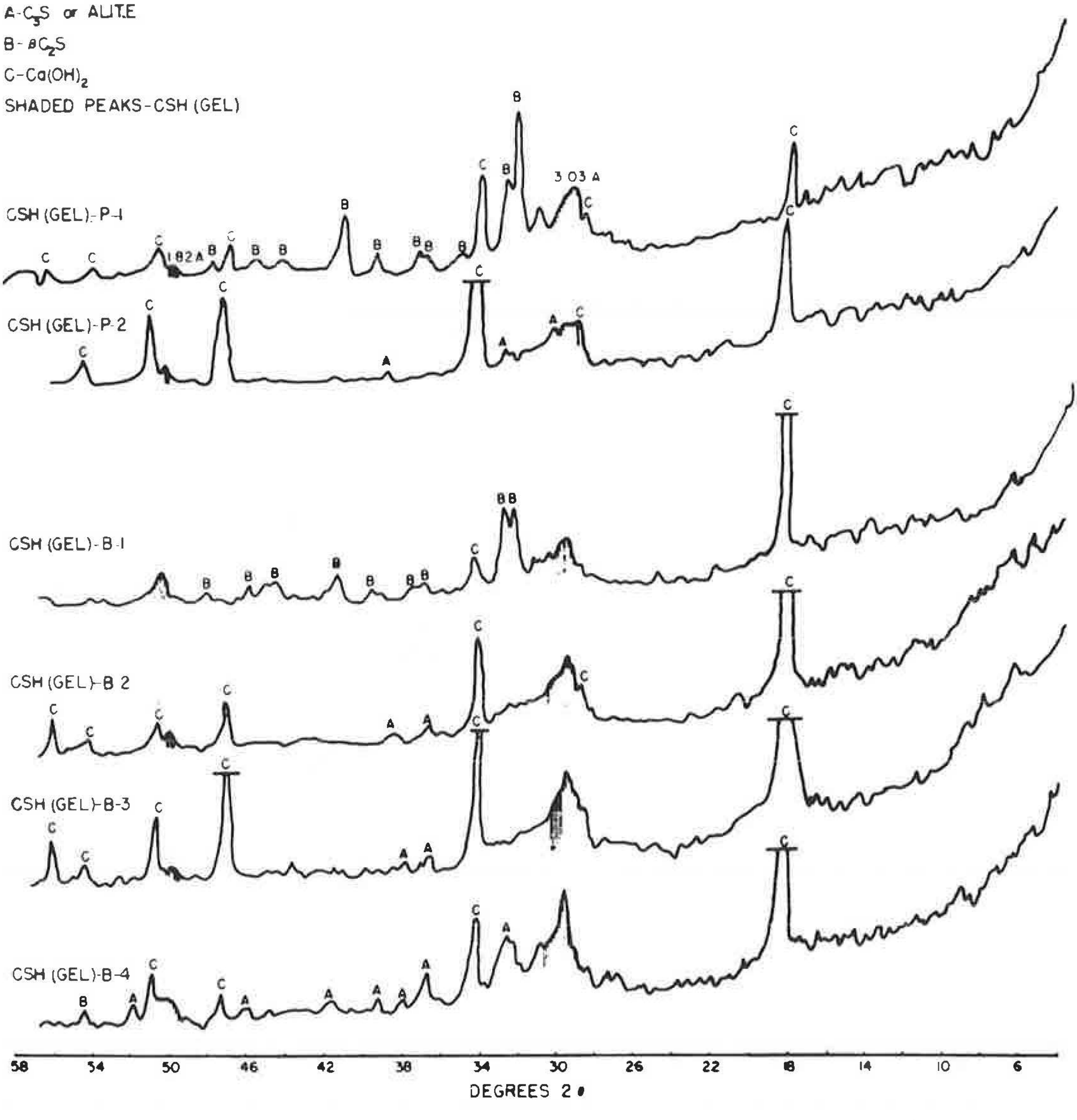


Figure 2. X-ray diffractometer traces for tobermorite gel products.

Attempts were made to obtain estimates of the basal spacings of CSH(I) preparations by use of oriented aggregate specimens. These were prepared by sedimentation after ultrasonic dispersion treatments, the sedimentation onto glass slides being carried out in vacuo over ascarite (to prevent carbonation). The results were disappointing. Broad, shallow peaks in the 10 to 14 A region were observed, but peak positions were indefinite and reproducibility was poor. The difficulty was not due to the existence of a random collection of mixed-layer hydration states in the material, because oven drying did not improve the patterns. It was apparent that dispersion to primary particles was not attained, and that the particles settling on the glass were themselves aggregates of cemented particles in random crystallographic orientation. In contrast, it was found that well-crystallized synthetic tobermorite dispersed to primary particles spontaneously even without ultrasonic treatment, and deposited films showed excellent orientation.

X-ray diffractometer traces for powder mounts of the tobermorite gel products described in Table 2 are shown in Figure 2, in which peaks attributable to the gel phase are shaded. It appears that x-ray diffraction is not a particularly fruitful tool for studying the characteristics of the gel phase in systems of hydrating cement constituents, because, in general, the CSH peaks are even broader and less intense than those of the CSH(I) preparations.

The pattern for the paste-hydrated β-C_2S, gel-P-1, shows that a relatively large amount of unreacted β-C_2S remains and only small peaks for $Ca(OH)_2$ are observed. The paste product derived from C_3S, gel-P-2, has produced much more $Ca(OH)_2$, and almost all C_3S seems to have reacted. These observations are in accord with expectation.

The four remaining patterns for bottle-hydrated material. All show strongly enhanced $Ca(OH)_2$ basal peaks. Much of the lime is present in large, well-formed crystals that orient preferentially despite efforts to prevent this in the powder sample preparation. β-C_2S seems to hydrate slowly even under the bottle-hydration conditions, the pattern for gel-B-1 showing that a good deal of the original compound is unreacted. The C_3S bottle-hydration product, gel-B-2, and one of the alite products, gel-B-3, have reacted almost completely, but the other alite, which has a relatively high content of MgO, does not seem to have reacted to as great an extent.

Hydrated cement phases do not usually yield basal peaks (2); however, basal reflections were secured in at least one preparation. Figure 3 is a trace of the C_3S bottle-hydration product, prepared as an oriented aggregate on a porous tile mount (12). A 14 A basal spacing with a second order peak at 7 A is clearly visible. Efforts to prepare similar mounts for the other materials were not as successful.

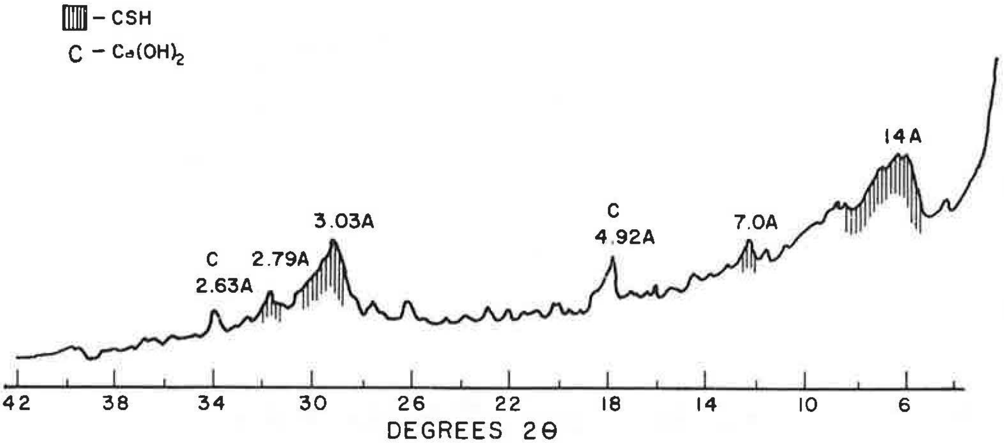


Figure 3. X-ray diffractometer trace for moist gel B-2 sample prepared as an oriented film.

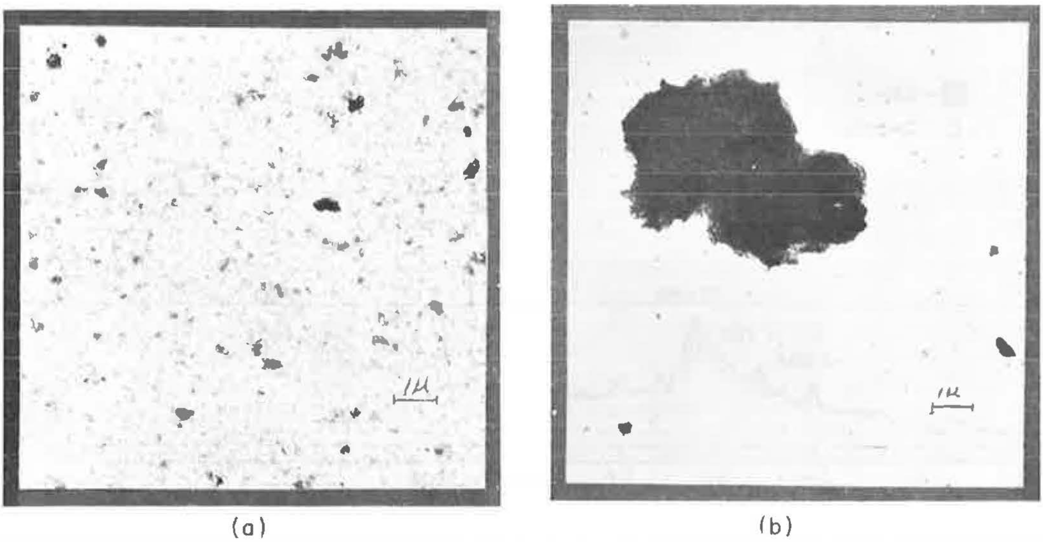
PARTICLE MORPHOLOGY

Electron microscopic study of some of these materials was carried out using an RCA EMU-3 instrument operated at 50 kvp. The sample preparation procedure used represents a departure from the usual techniques, in that dispersion was achieved using a nonaqueous system without ultrasonic vibration. This technique precluded the usual clumping together of particles that occurs on drying an aqueous suspension and revealed the morphology of the individual particles. All the electron micrographs were taken at a direct magnification of 4400 x.

Samples CSH(I)-5, 6, and 7 were examined by the electron microscope. Sample CSH(I)-5 (Fig. 4a) occurred primarily as extremely thin foils or "snowflakes." A few fields showed a greater proportion of thicker, irregularly shaped aggregates. The product gave a distinct strong polycrystalline electron diffraction diagram consisting of three perfectly smooth rings corresponding to the three main CSH(I) peaks noted on x-ray diffraction. CSH(I)-6 occurred in particles having more definite outlines. The individual particles appeared to be aggregates of twisted plate-like material. A few large aggregates were found, such as that shown in Figure 4b; this is identical in appearance to Figure 1 of Kalousek and Prebus (6). CSH(I)-7 was similar to CSH(I)-6, except that a larger proportion of the material was in fine foil-like condition, and the coarser particles seemed to be more definitely plate-like.

Electron micrographs of paste-hydrated C_3S revealed that most of the particles were fibrous, with the remainder being more or less equant in appearance; the latter may actually be bundles of fibers, but this was not evident. In addition, there were a number of thin sheet-like particles visible that showed no tendency toward rolling up into tubes or fibers. Figure 5a, a representative view of the bottle product of the C_3S, reveals that the particles in this product seem to be completely fibrous. A few bundles of undisturbed fibers are clearly visible.

Figure 5b shows the product designated gel-B-1, resulting from the bottle-hydration of β-C_2S. According to Copeland and Schulz (7), Brunauer and Greenberg (2), and others, such a preparation commonly yields CSH(II) with a distinctive cigar-shaped fiber bundle morphology and a slightly different x-ray diffraction pattern than tobermorite gel. However, in the present case it appears that tobermorite gel rather than CSH(II) has been formed.



(a) (b)

Figure 4. Electron micrographs: (a) CSH(I)-5, and (b) large aggregate in CSH(I)-6.

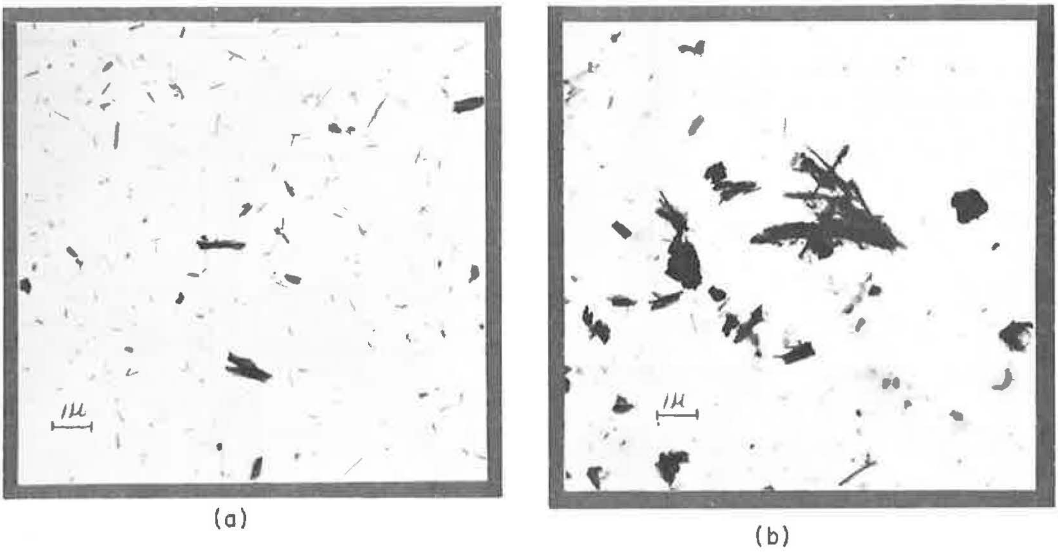


Figure 5. Electron micrograph: (a) gel B-2, from bottle hydration of C_3S, and (b) gel B-1, from bottle hydration of β-C_2S.

DIFFERENTIAL THERMAL ANALYSIS

Unfortunately, the comparison of DTA results for CSH(I) and tobermorite gel preparations is complicated by the fact that two different differential thermal units were used. The CSH(I) products were examined with a self-recording apparatus capable of maintaining a linear rate of temperature increase; 10 C was used. Through necessity, the gel materials were examined with a modified commercial portable DTA unit (Eberbach Corp., Ann Arbor, Mich.) which requires manual recording of the temperature differentials, and which does not maintain a linear heating rate. The modification involved replacement of the Transite insulating unit supplied with the equipment by a tight-fitting sleeve of commercial heating pipe insulation. As a result of this improved insulation, temperatures in excess of 1000 C could be readily obtained and the heating rate in the high-temperature region was speeded up enough so that the DTA record in this area was useful. The measured heating rate was constant at 58 C/min from room temperature to about 600 C; above this temperature, it decreased to 5 C/min at 1000 C. Several check runs showed that although peak temperatures were not exactly comparable to those secured on more standard laboratory instruments, the deviations were not overly large; peak shapes were, in general, preserved.

DTA results for three of the CSH(I) samples are shown in Figure 6. The major feature is the sharp, strong exothermic reaction marking the transformation to wollastonite at 825 C for the first two specimens and 860 C for the last. All specimens show a strong low-temperature dehydration endotherm, a distinct endothermic dip at about 790 C just before the exotherm, and a faint endothermic deflection at about 665 C. In securing these patterns it was observed that considerable shrinkage occurred at the temperature of the strong exotherm, yielding a soft and somewhat friable product which gave an x-ray pattern for wollastonite. A similar strong exothermic response was shown by aluminum-substituted tobermorite (13), but in the latter case the product was hard and well-cemented.

DTA results for some of the tobermorite gel samples are shown in Figure 7, the patterns having been secured with the portable instrument. The patterns shown are all much alike. They display a strong low-temperature endotherm due to release of adsorbed water, a strong endotherm at about 570 C due to the dehydroxylation of lime formed in the hydration reaction, and a small but sharp high-temperature exotherm at about 860 C. In the bottle-hydration products, there is a small endothermic break in

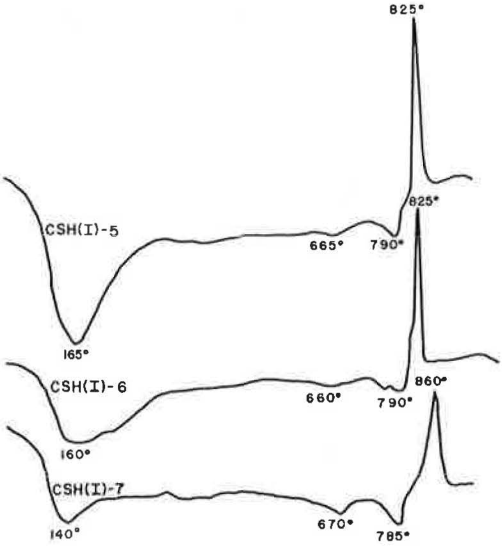


Figure 6. DTA of CSH(I) samples, heating rate 10 C/min.

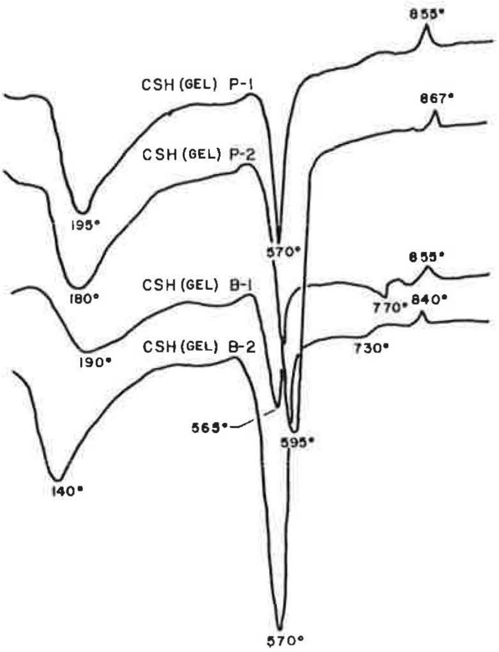


Figure 7. DTA of tobermorite gel products, heating rate from 58 to 5 C/min.

the 750 C zone which may be characteristic of the CSH or may be the result of a trace of carbonation. DTA results for bottle-hydration products of the two alite samples (not shown) closely resemble that of the corresponding C_3S sample. In fact, the basic similarity of the patterns for all the gel products (except for the effects of the varying amounts of lime generated) is noteworthy; this similarity offers support for the concept of tobermorite gel as a distinct and fairly uniform phase, irrespective of the starting mineral or the particular mode of hydration used in its preparation. The distinction between tobermorite gel and CSH(I) on the basis of the difference in intensity of the high-temperature exotherm also seems to be consistent and reliable.

INFRARED SPECTROSCOPY

Infrared spectra of poorly crystallized CSH have been published by several workers, including Kalousek and Roy (14), Hunt (15, 16), Lehmann and Dutz (17, 18), and Midgley (19). All have used the KBr pellet technique, involving preparation of a transparent pellet by pressure exerted on a mixture of the sample with a large excess of powdered KBr. Because one of the most useful results of infrared examination is an indication of the state of water in the system, and because KBr in powder form is hygroscopic, tending to adsorb and retain traces of water vapor even on evacuation and oven drying, it was thought desirable to avoid this technique. A simple procedure was evolved in which the sample was mulled briefly with spectral-grade CCl_4 and the resulting suspension pipetted onto the plane surface of a polished KBr plate that had been dried and kept at about 60 C in an oven. The CCl_4 evaporated in a minute or so, leaving a deposit of CSH sample on the KBr disc. This provided a useful and reproducible spectrum. Some skill was found to be required to avoid the deposition of too much or too little sample, but because an incorrectly prepared specimen could be washed off in CCl_4 and a new one prepared in a few minutes, satisfactory results were readily obtained.

CSH(I) spectra were run on a Perkin-Elmer 421 dual-grating spectrophotometer, but the gel samples were examined using a Perkin-Elmer 221 instrument. The former produces a chart linear in wave number, the latter one linear in wavelength; resolution and other features of the instruments are comparable. The 5 x scale expansion feature was used for all patterns.

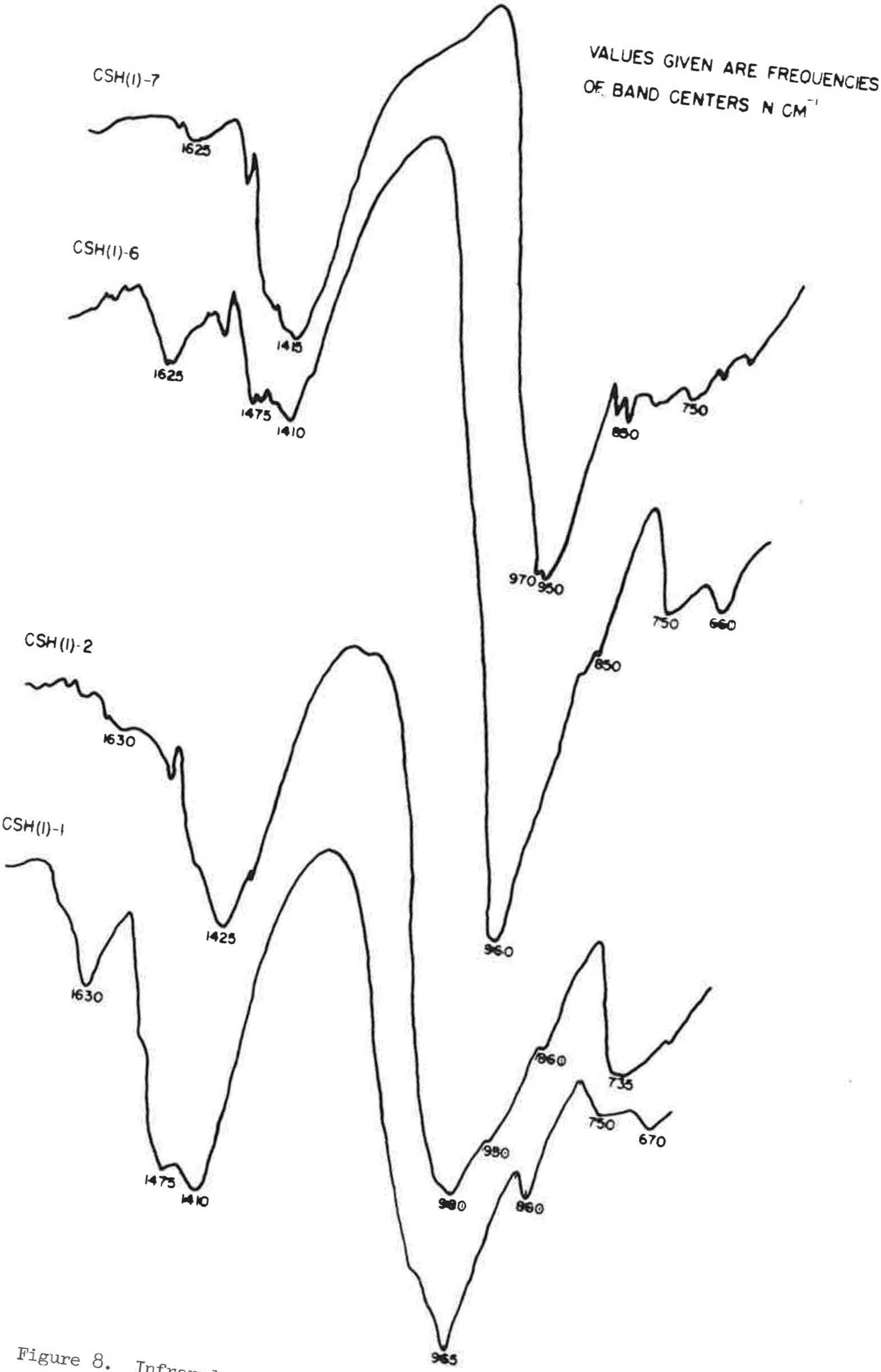


Figure 8. Infrared absorption spectra for CSH(I) samples.

Portions of the spectra of four of the CSH(I) samples are shown in Figure 8. The "hydroxyl region" is not shown, but in each case the hydroxyl stretching vibration band consisted of a broad, shallow trough centered at about 3400 cm^{-1}, a position characteristic of vibration of hydrogen bonded OH groups; in no case was a band observed in the "free" OH stretching vibration region at about 3700 cm^{-1}. This suggests that free (non-hydrogen-bonded) hydroxyl groups are not present in these materials. Also, the strengths of the hydroxyl stretching bands in these patterns were only about 10 to 15 percent of the strengths of the main Si-O lattice vibration band. Previously published results, in which the KBr pellet technique was employed, generally showed much stronger hydroxyl bands relative to their Si-O bands.

In Figure 8, the band at approximately 1630 cm^{-1} is the bending vibration of water, in this case water present in the CSH(I); the large band between 1400 and 1500 cm^{-1} (split in some of the material) is probably due to the asymmetrical stretching mode of the carbonate ion (15); presumably the carbonate was present as a result of carbon dioxide reaction with the surface of the CSH(I). The band for sample CSH(I)-1, which displayed vaterite x-ray diffraction peaks, was not appreciably stronger than those for the other samples. Hunt (15) has shown that a very small percentage of carbonate can produce a disproportionately large effect on the infrared spectrum, and this has been confirmed in laboratory trials. The major band at about 970 cm^{-1} is the main Si-O lattice vibration effect previously mentioned. The small band at about 860 cm^{-1} may be the out-of-plane bending vibration of the carbonate group, although this is usually recorded at about 890 cm^{-1} (20). Infrared spectra for the other CSH(I) samples, not shown, are similar to that shown for CSH(I)-6, which may thus be considered typical of the group as a whole.

Certain specific details of the individual patterns should be pointed out. First, the infrared spectrum for CSH(I)-2, the x-ray-amorphous member of the group, is similar to those of the other samples. A second point is the weakness of the water bending mode at about 1625 cm^{-1} in some samples; it is almost absent in CSH(I)-2 and CSH(I)-7 despite the high structural water content of these samples. A third observation is that the exact position of maximum absorption for the Si-O lattice vibration band varies somewhat from sample to sample, from perhaps 950 cm^{-1} (portion of a split peak in CSH(I)-7) to as high as 980 cm^{-1} for CSH(I)-2. Lehmann and Dutz (17) suggested that similar differences in the spectra of the hydration products of the cement minerals may indicate variation in the degree of polymerization of the silica tetrahedra making up part of the framework of the mineral, increasing degree of polymerization being marked by higher wave numbers (shorter wavelength). A systematic study of this point may be of considerable importance in clearing up details of the structure of the CSH(I) phase. A final feature of interest is the pronounced minimum in absorption in the region of about 1150 to 1200 cm^{-1}. This feature is even more pronounced with tobermorite gel spectra.

Spectra for five of the products of the hydrated cement minerals are shown in Figure 9. Because these spectra were secured using an instrument the presentation of which is linear in wavelength rather than wave number, peaks at lower wave numbers are broader and more diffuse than they would be on the instrument used for the CSH(I) spectra.

The most obvious feature of the tobermorite gel spectra is the very strong minimum in absorption at about 1200 cm^{-1}, stronger and more pronounced than the corresponding effect with the CSH(I) materials. The prominence of the effect is not due to the particular instrumentation employed because the 421 instrument gave an identical effect. The effect is not apparent in previously published spectra of gel products in which the KBr pellet procedure had been employed. This minimum is thought to be attributable to the Christiansen filter effect, which is known to occur with powdered solids suspended in a fluid (in this case, air), and has been demonstrated in infrared spectroscopy on various classes of material (21, 22). Briefly, the Christiansen filter effect is due to a wide variation in the index of refraction of certain particulate solids with wavelength in the region of a strong absorption band. At a wavelength slightly shorter than that of the absorption band, the index of refraction of the solid may match that of the fluid, and at this point scattering by multiple reflection and refraction at the many powder-fluid interfaces is at a minimum; consequently, a pronounced minimum in absorption is observed.

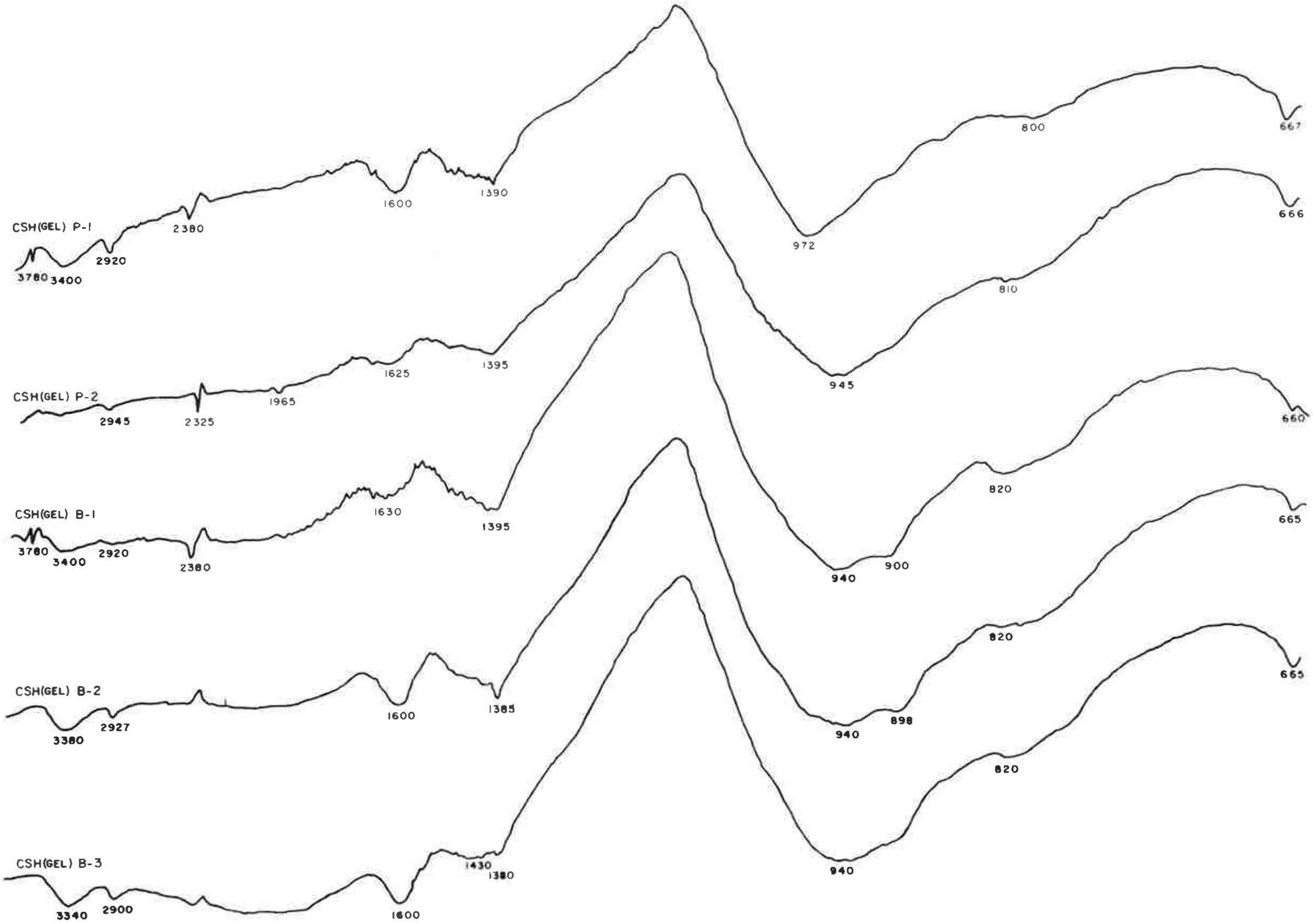


Figure 9. Infrared absorption spectra for tobermorite gel products.

The strong absorption band here is the Si-O lattice vibration feature; this occurs at about 940 cm^{-1}, except for the paste-hydration product of β-C_2S for which the position is apparently 970 cm^{-1}. The theoretical absorption band cited by Lehmann and Dutz (17) for completely unpolymerized silica tetrahedra (i.e., an orthosilicate) is 935 cm^{-1}; the closeness of the observed positions to this figure seems to imply that, in agreement with the views of Brunauer and Greenberg (2), the tobermorite gel tends to be largely an orthosilicate.

The band itself is somewhat broader and less marked than the corresponding CSH(I) feature. Secondary maxima of obscure origin are observed at about 820 and 900 cm^{-1} in most of the samples. Small bands occur at 1600 to 1630 cm^{-1} (presumably due to the water bending vibration) and near 1400 cm^{-1} (probably indicating some carbonation has taken place). If these bands are interpreted correctly, one would suppose from the appearance of the patterns that these samples retained somewhat more water and had somewhat less carbonate than the CSH(I) samples discussed previously. Also, the wave number of the band attributable to the carbonate ion is distinctly lower in the present spectra, suggesting that the carbonate ions are held more tightly in the tobermorite gel samples than in CSH(I).

In Figure 9, a number of small features can be observed in the 2000 to 4000 cm^{-1} region. A comparatively weak and broad band is observable at 3340 to 3400 cm^{-1}, which is the OH stretching vibration for hydrogen-bonded OH groups. Patterns for both paste- and bottle-hydrated samples derived from β-C_2S show a sharp, complex absorption feature at 3780 cm^{-1}; and all samples show additional small, sharp features at around 2900 cm^{-1} and between 2300 and 2400 cm^{-1}, the causes of which are uncertain. In general the spectra are all similar to each other, and sufficiently different from the CSH(I) materials that one can readily distinguish them from that phase.

WATER-VAPOR ADSORPTION AND SURFACE AREA

Water-vapor adsorption isotherms at 21 C were secured in order to characterize the CSH(I) samples. In view of the many water-vapor surface area measurements of tobermorite gel products by other workers, and in view of the experimental difficulties involved in correcting for the presence of lime and residual unhydrated material, sorption measurements for the gel materials were not attempted.

The procedure involved outgassing over P_2O_5 at room temperature for 4 days, then equilibration over concentrated sulfuric acid solutions of successively lower concentration. The concentration of each solution was determined by titration after equilibration, and the partial pressure of water vapor was determined from this. For each sample, at least five points were secured in duplicate in the BET range, and a more extended set of determinations was made with one. The surface areas were computed using an assigned area of 11.4 sq A/water molecule (2), and an estimate of the heat of adsorption of the uniform portion of the first layer, E_1, was calculated according to the BET procedure (23).

The quantitative results for these determinations are given in Table 3. The approximate range in surface area for the CSH(I) materials was 150 to 350 sq m/gm; these limits are consistent with the range of 135 to 380 sq m/gm cited recently by Brunauer (24). This range is similar to that usually found for tobermorite gels. The first four samples, prepared by rapid precipitation without any particular opportunity for aging, were significantly higher in surface area than the others. However, there does not seem to be a relationship between high surface area and poor crystallinity: CSH(I)-2, the x-ray-amorphous sample, has by far the poorest degree of crystallinity, yet it occupies the median position with respect to surface area.

The measured E_1 values range from about 12,500 to over 13,500 cal/mole; that is to say, the difference between E_1 and the bulk heat of condensation of water vapor is generally of the order of 2,000 to 3,000 cal/mole. It is noteworthy that the x-ray-amorphous samples have an unusually low E_1, which is only about 1,200 cal/mole higher than the heat of condensation of water.

A reduced water-vapor adsorption isotherm for six of the seven materials is given in Figure 10. The relative concordance of all data plotted in this way (which removes

TABLE 3

SURFACE AREAS AND HEATS OF ADSORPTION OF WATER VAPOR[a]

Sample No.	Surface Area (sq m/gm)	E_1 (cal/mole)
CSH(I)-1	355	12,700
CSH(I)-2	245	11,700
CSH(I)-3	280	12,800
CSH(I)-4	300	12,500
CSH(I)-5	165	13,100
CSH(I)-6	175	13,700
CSH(I)-7	155	12,700

[a] For CSH(I) preparations at 21 C.

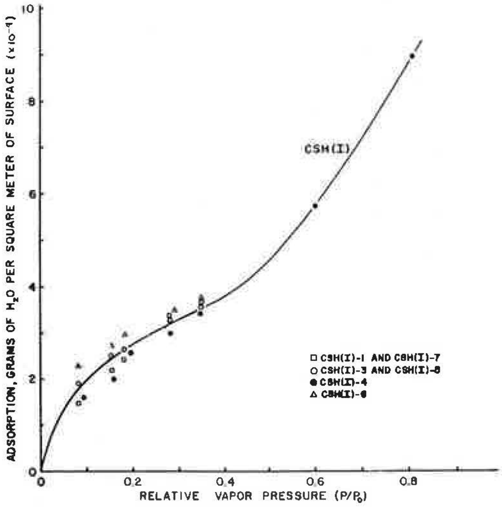


Figure 10. Reduced water vapor adsorption isotherm for CSH(I) samples.

the effect of the differing surface areas of the individual samples) suggests that the samples for which points are plotted have surfaces qualitatively similar at least with respect to the sorption of water vapor. The isotherm is clearly a standard BET type II, and no particular restriction on the number of layers that can be adsorbed seems to occur.

The data for the x-ray-amorphous sample (not plotted) fall far below the line for the other samples. This is not surprising in view of the low E_1 value calculated for this material, and the two facts suggest that the surface of the amorphous sample has a relatively weak attraction for water vapor compared to the surfaces of the better-crystallized CSH(I) samples.

SURFACE CHARGE

Attempts were made to measure zeta potentials of both CSH(I) and tobermorite gel samples by means of the standard flat-cell microelectrophoresis apparatus (25). These attempts were unsuccessful, however, owing to an inability to achieve a satisfactory degree of dispersion. Even after continued ultrasonic treatment for long periods, the particles occurring in water suspension were aggregates that settled to the bottom of the microelectrophoresis cell so rapidly that horizontal particle velocity could not be measured under influence of the applied electric current. However, because the direction of travel of the particles could readily be determined, the sign of the net surface charge could be obtained.

The CSH(I) particles dispersed in distilled water were charged negatively, but the same materials dispersed in saturated calcium hydroxide solutions were charged positively. The tobermorite gel samples initially dispersed in water were positively charged, but in view of the calcium hydroxide present as a companion product of the hydration reactions, this result was not unexpected. When the gel products were washed repeatedly in distilled water to remove the accompanying calcium hydroxide, the positive charge was visibly decreased as the pH of the suspension was reduced, and at a pH of about 10 the sign of the surface charge became negative. Thus, the basic observations of Stein (26) on tobermorite are apparently applicable also to CSH(I) and tobermorite gel. The sign reversal did not appear to influence the state of aggregation of the particles; the colloidal aggregates remained well-cemented regardless of the charge.

CATION EXCHANGE CAPACITY MEASUREMENTS

The idea that tobermorite and perhaps the poorly crystallized tobermorite-like CSH might have distinctive cation-exchange properties is not new; speculations to this effect were given by McConnell (27) and by Roy (28). However, no laboratory confirmation of such properties can be found. One difficulty is that, due to the small but not negligible solubility of these phases in water, the methods normally employed for cation exchange determinations are untrustworthy. The difficulty is that after treating the sample with solutions containing a large excess of a measuring cation to insure replacement of the original cations on the exchange sites, all excess measuring cation must be removed. This is usually accomplished by repeated washing. However, repeated washing of CSH(I) and tobermorite gel with water leads to breakdown and eventual dissolution of the sample. This liberates calcium ions, which exchange with some of the measuring cations adsorbed on the exchange sites, thus invalidating the determination.

After a good deal of experimentation, a method was devised to obviate this difficulty (29). Potassium ions were used as the measuring cations with absolute ethanol as the solvent and washing medium. The potassium was added as a 1 N solution of potassium acetate in ethanol. After overnight equilibration and repeated treatments with fresh solution to insure complete exchange, the excess potassium acetate was removed by repeated washing in ethanol. After five such washing treatments, the potassium remaining, exchanged potassium, was in turn replaced by either sodium or ammonium ions derived from repeated additions of solutions of the corresponding acetate in ethanol. The washings containing the released potassium were combined, diluted, and the potassium content determined by flame photometry.

The polyethylene centrifuge tubes used for the saturation and washing treatments adsorbed and retained a small quantity of potassium against washing, and a blank correction for this effect was required. Furthermore, use of ammonium acetate to replace exchanged potassium in some cases resulted in the formation of a gel, which made the necessary washing treatments mechanically difficult. Use of the sodium salt met no such handicap, but unfortunately sodium acetate is far less soluble in ethanol than is the ammonium salt.

A check of the method with unfractionated Volclay-brand Wyoming bentonite yielded a value of 85 meq/100 gm, in good agreement with more conventional determinations.

Cation-exchange capacities for five of the seven CSH(I) samples were determined. Values obtained using sodium acetate as the replacing salt ranged from 4 to 24 meq/100 gm. The exchange capacities do not appear to be related to either the surface area or any other measured characteristic of the samples. Similar determinations were carried out on some of the tobermorite gel materials with ammonium acetate used as the replacing salt. These values were of the same order of magnitude, the bottle-hydrated C_3S product yielding the low value of 7 meq/100 gm and the paste product of the same material yielding the high value of about 20 meq/100 gm. The bottle-hydrated alites both gave values somewhat higher than the corresponding bottle-hydrated C_3S product, both hydrated alite samples giving 18 meq/100 gm. Separate measurements were made on calcium hydroxide and on the cement minerals, C_3S, alite, and β-C_2S. Of these, a zero exchange capacity was recorded for the lime, and exchange capacities of about 3 meq/100 gm were recorded for each of the others. Thus, the observed exchange capacities of the gel samples relate primarily to the tobermorite gel per se, and not to the accessory constituents present.

DISCUSSION AND CONCLUSIONS

As a result of parallel studies on CSH(I) samples and on the hydration products of cement minerals, the CSH(I) phase and the tobermorite gel phase appear to be distinctive entities with only limited ranges of variation in properties despite the wide compositional range of the former. The gel materials produced by paste and by bottle hydration of β-C_2S, C_3S, and alite were all remarkably similar to each other. These phases are distinct from well-crystallized tobermorite not only in their poor crystallinity but also in a number of other ways.

One of the notable differences found between the tobermorite gel, CSH(I) materials, and tobermorite is that the particles of the former two materials are inherently cemented to form aggregates that resist dispersion. This cementation seems to be unaffected by the zeta potential of the material; at least changes in surface charge from strongly positive to strongly negative do not result in any noticeable tendency for the aggregated particles to disperse. This feature is as pronounced with CSH(I) as it is with tobermorite gel. A corollary to this observation is the discovery (30) that when CSH(I) is produced by reaction of calcium hydroxide on clay minerals, cementation is as effective and permanent as when tobermorite gel is produced under similar circumstances. These results point to the importance of the chemical factor in cementation.

The present results confirm, and to some extent supplement, earlier results relative to x-ray diffraction, DTA, morphology, and infrared behavior of these materials. One of the chief benefits is that all these results are available for the same well-defined group of samples.

The observed cation-exchange properties of these materials are not easily explainable in terms of isomorphous substitution, because most of the samples are pure CSH. The other commonly accepted source of cation-exchange sites in silicate minerals is so-called "broken-bond" sites arising at the edges of the particles. However, in view of the lack of knowledge of the detailed structure of these CSH, speculation as to the location of the exchange sites seems to be premature.

The results point to a number of differences in the properties of CSH(I) and tobermorite gel that may be useful for identification. X-ray diffraction is felt to be inadequate for the purpose, but the DTA pattern seems to be diagnostic; CSH(I) always produces a strong, sharp, high-temperature exothermic response, whereas tobermorite gel always produces a much less intense exotherm at about the same position. The morphologies of the two phases are distinct, CSH(I) having a snowflake, thin plate-like, or crinkled foil appearance, whereas tobermorite gel is essentially fibrous. Infrared spectra are of some utility in identification of the phases, the patterns for the gel of whatever origin being broader and more diffuse than those for CSH(I). For samples prepared in the manner employed in the present work, the sharpness and intensity of the absorption minimum is uniformly more pronounced for the gel materials; this may be of diagnostic utility.

Finally, attention is drawn to the failure to produce CSH(II) by the method described by Toropov et al. Independent confirmation of this synthesis is apparently still lacking.

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Studies of Early Hydration Reactions of Portland Cement by X-Ray Diffraction

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Monitoring by X-ray diffraction of hydration of tricalcium aluminate in pastes containing calcium hydroxide and gypsum has demonstrated successive formation of the high-sulfate form of calcium sulfoaluminate hydrate (ettringite), the low-sulfate form of that compound, and finally, a solid solution of the low-sulfated hydrate and tetracalcium aluminate hydrate. These reactions and effects of various factors on them correspond very closely to the early hydration behavior of C_3A in portland cement. Diffraction studies of hydrating sintered tricalcium aluminate slabs have demonstrated the retarding effect of the initially formed ettringite film. X-ray and dilatometer studies have shown that the hydrating C_3A pastes undergo large increases in volume because of a tendency to imbibe large quantities of water. The individual effects of other portland cement constituents on these hydration reactions have been investigated.

A study of hydration of combinations of the various constituents has led to a fairly complete picture of the early hydration reactions of portland cement. Examination of a few well-known accelerating and retarding materials has shown them to affect primarily the hydration rate of C_3S. They may affect the rates but not the nature of the early C_3A reactions. Retarders can produce a large initial acceleration of C_3A hydration. When considered in relation to the state of the calcium sulfate in the cement, this previously unrecognized effect can account for many instances of abnormal setting of concrete. Optimum SO_3 content is characterized by gypsum depletion at 18 to 24 hr after gaging. Higher SO_3 contents cause water imbibition to produce excessive expansion and lowered strength. This water imbibition is a major factor in the behavior of shrinkage-compensating and expansive cements.

•MANY MODERN methods of concrete construction involve conditions of use affecting the early hydration reactions of portland cement. Various means are used to produce acceleration or retardation of set, enhancement of rate of early strength development, and variations in workability and water requirement of concretes made from a given cement. These practices result from the increasing production of concrete under unusual conditions such as extremes of temperature and also from the ever-increasing interest in the use of chemical admixtures to modify concrete characteristics (1).

Accompanying these practices, there are developing an increasing number of problems relating to the performance of the concrete. Some of these are caused by improper use of concreting materials. Others appear to result from unusual and unexpected behavior exhibited by particular cement-admixture combinations. In numerous instances the causes of the observed behavior are not understood, and corrective measures must be developed empirically.

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A fundamental approach to solutions of these problems requires a knowledge not only of the early hydration reactions of portland cement but also of the effects of various factors on these reactions and, further, of the effects of variations in these reactions on the ultimate properties of the concrete. The work of Lerch (2) on the effect of SO_3 content on the properties of hydrated cement is a landmark in this area. The existing scientific knowledge of pure cement components was applied to a study of the effects of cement composition on the rates of early hydration and also on some of the important engineering properties of concrete. The effect of variations of SO_3 content on the early hydration of cements with various compositions was clearly demonstrated. Equally clear was the demonstration that changes in SO_3 content and in the rates of hydration affected the engineering properties studied. A more recent paper by Klieger (3) demonstrates analogous results as regards the effect of placing and curing temperature on strength development.

The implications of Lerch's work have not yet been fully explored. For instance, it seems reasonable to suppose that the use of chemical admixtures known to have an effect on the rates of early hydration would, as in the case of gypsum, affect the ultimate concrete performance. Because of the problems encountered in recent years, there is presently a definite need for a better understanding both of the early hydration reactions and of the effects of deliberate changes in the early reaction rates. Lerch based his conclusions primarily on the effects of cement composition on the early reaction rates as measured by rates of heat evolution. He was thus able to avoid involvement in the existing uncertainties concerning the nature of the hydration reactions and reaction products occurring in cement pastes with the water contents used in concrete. Resolution of these uncertainties would add greatly to the ability to control and interpret concrete performance.

The present paper is a progress report covering a large volume of work on the application of specially developed X-ray diffraction techniques (4) to supplement the earlier results of calorimetry, microscopy, and chemical analysis by direct observations of changes in composition and structure of hydrating solid phases.

A detailed examination was made of the hydration of tricalcium aluminate in low-water-content pastes containing solid calcium hydroxide and gypsum.

MATERIALS AND TECHNIQUES

Aluminates

Various methods of preparing tricalcium aluminate have been compared. The method found most effective was based on an observation by Schneider and Thorvaldson (5). In this method, an appropriately proportioned mixture of calcium hydroxide and aluminum hydroxide was autoclaved to produce the cubic C_3AH_6. (Symbols used in cement chemistry are as follows: C = CaO, A = Al_2O_3, S = SiO_2, F = Fe_2O_3, N = Na_2O, H = H_2O.) The product was then fused at 1410 C. The free lime content of the product was 0.2 percent. It is thus possible to produce this material with only one fusion. The fineness of grinding and possibly the method of preparation have a profound effect on the reactivity of the product. The rates of reaction for different batches varied widely. As a consequence, the behavior of complex mixtures was correspondingly variable in time of development of new phases, in rate of heat development, and in setting time. The results reported here are necessarily limited to comparisons between hydration stages of the same materials or between different compositions made from portions of the same batch of C_3A.

For the preparation of sodium calcium aluminate (NC_8A_3), a mixture of calcium oxide and aluminum oxide in a mole ratio of 5:3 was heated to its melting point. A mixture of the product with appropriate proportions of tricalcium aluminate and sodium carbonate was then fused. The resulting solid was ground to pass a 200-mesh screen and then heated to fusion again. The heat treatment resulted in a loss of alkali by volatilization. The final product, therefore, contained only 6.6 percent Na_2O as compared with the theoretical 7.6 percent. For the purposes of this study, this deficiency of alkali is unimportant.

Ferrites

The ferrites C_2F, C_6AF_2, and C_6A_2F were prepared as described in the literature (6). The compound C_4AF was prepared in the same way as the tricalcium aluminate described previously, except for inclusion of an appropriate quantity of ferric hydroxide in the raw material.

Tricalcium Silicate

The tricalcium silicate was prepared by a method described in the literature (7).

X-Ray Diffraction

All X-ray diffraction work was carried out with copper Kα radiation on a Norelco Geiger counter diffractometer modified to provide temperature and ambient atmosphere control of the sample, as has been described in a previous paper (4) that also describes the monitor techniques used. Most X-ray scanning was done at a rate of 1° 2θ/min with 1° divergence and receiving slits, a 0.003° scatter slit, and a time constant of 4 sec.

No special precautions were taken to avoid preferred orientation of the powdered samples. As a result, individual lines in patterns of duplicate samples of the same material exhibit small random variations in intensity. This random variation is necessarily a component of changes observed in diffraction patterns of different hydration stages, either of different samples of the same material or of the same sample after smoothing, such as are shown in the figures. These variations could be clearly distinguished from the intensity changes described in the text as indicating changes in compositions only after examination of large numbers of individual patterns.

In some instances it became necessary to distinguish between di- and tetracalcium aluminate hydrates. At water saturation, these phases are present as C_2AH_8 and C_4AH_{19}, both of which have a first order diffraction at $2\theta = 8.3°$. A method of identification was developed, based on work of Roberts (8). In this method, dry nitrogen is admitted to the diffractometer scatter shield through the atmosphere control system. The ensuing dehydration of the sample produces line shifts from 8.3° for saturation compounds to 10.2° and 11.2° for C_2AH_5 and C_4AH_{13}, respectively.

Temperature Control

All work was carried out at room temperature unless otherwise indicated. Initially, reaction mixtures were frequently stored at 40 F to prevent conversion of the hexagonal tetracalcium aluminate hydrates to the cubic C_3AH_6. This precaution was later found to be necessary only for compositions free of sulfate ion. It has been verified that a very small quantity of sulfate ion stabilizes the hexagonal hydrates at temperatures up to 100 F. Previous investigators have uniformly found that C_3AH_6 crystallizes with difficulty, if at all, in compositions containing SO_3 (9). The relationship between the thermodynamic stability of the phases and the temperature has been demonstrated (4).

Volume Change

Tendencies toward volume changes during early hydration were measured with a dilatometer adapted from the osmotic cells previously used for studies of alkali-reactive aggregates (10). For this purpose, a cement membrane with a water-cement ratio of 0.75 was inserted into the cell in the usual way. A pat of the paste to be studied was trowelled on one side of the membrane. The cell was then assembled so that the half-cell containing the pat was full of mercury, while the other half-cell was full of water. If the pat imbibed water through the membrane, the mercury level rose and the water level fell. If, on the other hand, the pat contained excess water, the mercury pressure forced the water through the membrane, with a corresponding drop in mercury level and rise in water level. The results obtained were not quantitatively reproducible because the swelling tendency could be counteracted by the small mercury pressure present and because of the dependence of the water imbibition rate on the shape of the pat and the area exposed to the membrane. The reliance placed on the results obtained depends on the constancy of the levels after the reactions have ceased. This stability of the system indicates the absence of leaks and of extraneous reactions causing flow through the membrane.

Hydration of Sintered Slabs

A novel technique was developed for investigating the nature of hydration reactions on the surface of tricalcium aluminate. For this purpose aggregations of the powdered mineral were prepared by compaction and subsequent sintering at about 1400 C. The pats were formed as little slabs that fit into the diffractometer sample holder. After the surface was smoothed by filing, the pat was hydrated by immersion for some appropriate length of time. X-ray diffraction patterns were then made of the hydrated surface and of the surfaces remaining after thin layers of hydrated material were removed by grinding. By this technique, the nature and sequence of the hydration products could be ascertained.

Chemical Analysis

The conventional methods of chemical analysis of portland cement (11) were used in these studies. However, determinations of alumina in compositions high in both lime and alumina gave inaccurate results because of precipitation of part of the lime as calcium hydroxide in the R_2O_3 precipitate. This error was detected from analyses of pure compounds that yielded CaO/Al_2O_3 ratios consistently less than stoichiometric. Even a triple precipitation of aluminum hydroxide by the classical ammonia method carried down a considerable quantity of calcium. Successful separations were obtained by precipitation of the aluminum as the basic succinate (12).

The concentration of sucrose in solution was determined by a published method (13).

Lignosulfonate concentration in solution was determined by a modification of the spectrophotometric method of Ernsberger and France (14), whereby the final pH of the solution was adjusted to a value of 3.0 to avoid effects of acidity on optical density (15). Measurements were made at 360 mμ for low concentrations of 410 mμ for the higher range.

BASE MIXTURES AND THEIR HYDRATION

Purpose and Composition of Base Mixtures

In these studies, the fundamental reference point is the hydration behavior of a particular series of mixtures of synthetic compounds designated as base mixtures. All mixtures in the series contain tricalcium aluminate, calcium hydroxide, gypsum, and distilled water. In these mixtures, the C_3A and $Ca(OH)_2$ are present in equimolar quantities and the gypsum content is varied. The water-to-solids ratio is 0.4.

The compositions of the base mixtures were selected after a number of exploratory studies. The unit mole ratio for $Ca(OH)_2/C_3A$ stemmed from an observed enhancement of the retarding effect of gypsum by calcium hydroxide and also from a desire to allow formation of the highest limed hydrate, C_4AH_{19}. The water content was chosen low enough to produce a diffraction surface that would not be materially distorted by sedimentation.

The previously described special sample holders (4) were devised when it was found that the water-to-solids ratio of 0.4 frequently provided insufficient water for completion of the hydration reactions. The imbibition of water from the reservoirs in these holders caused distortion of the diffracting surface as the sample swelled. Restoration of the surface was accomplished by frequent manual smoothing.

The general hydration behavior of the base mixtures and the techniques used in interpreting the diffraction patterns can be most easily described by means of specific examples (Figs. 1 and 2). These illustrations, typical of the general pattern, show diffraction patterns at various ages for base mixtures with SO_3/Al_2O_3 mole ratios of $\frac{1}{4}$ and $\frac{3}{4}$, respectively, for a sample of C_3A with a specific surface of 3,100 sq cm/g (Blaine). The actual patterns shown here were not, however, produced by continuous

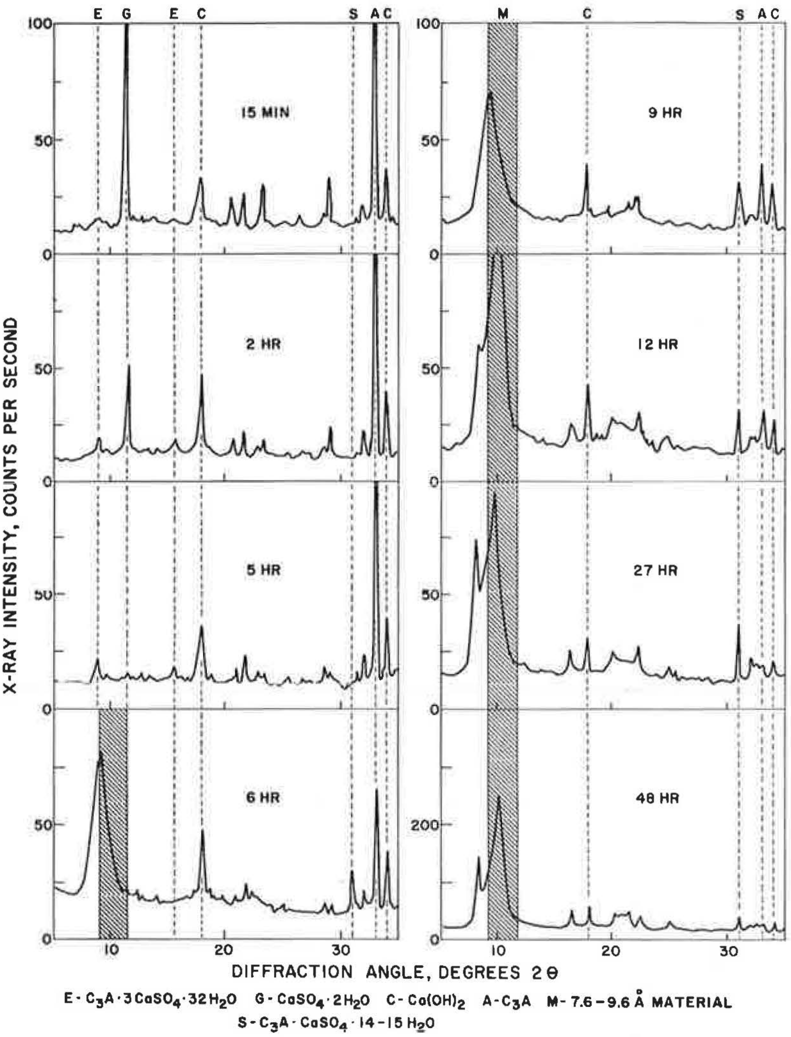

Figure 1. Diffraction patterns of base mixture with 1/4 mole SO_3 per mole alumina.

monitoring, because excessive carbonation would have resulted in distortion of the results at later ages. Several identical samples were hydrated simultaneously in the special sample holders in a sealed container, and care was taken to transfer only relatively uncarbonated samples to the diffractometer at the appropriate times. It has been found that continuous monitoring of samples for more than a few hours is feasible only during periods of rapid expansion; under these conditions the manual smoothing results in removal of carbonation products from the diffracting surface. In the following descriptions, as in the figures, locations of diffraction lines are designated in terms of degrees 2θ.

Hydration at Low Gypsum Content

In Figure 1 the pattern at 15 min indicates the presence of the raw materials by a very large C_3A peak at 33.1°, a gypsum peak at 11.6°, and a calcium hydroxide peak at 18.1°. In addition, slight lines are seen at 9.1° and 15.7° for the high-sulfate form of calcium sulfoaluminate hydrate ($C_3A \cdot 3\,CaSO_4 \cdot 31\text{-}33\,H_2O$) which, for simplicity, will be consistently referred to as ettringite. The pattern at 5 hr represents a transition

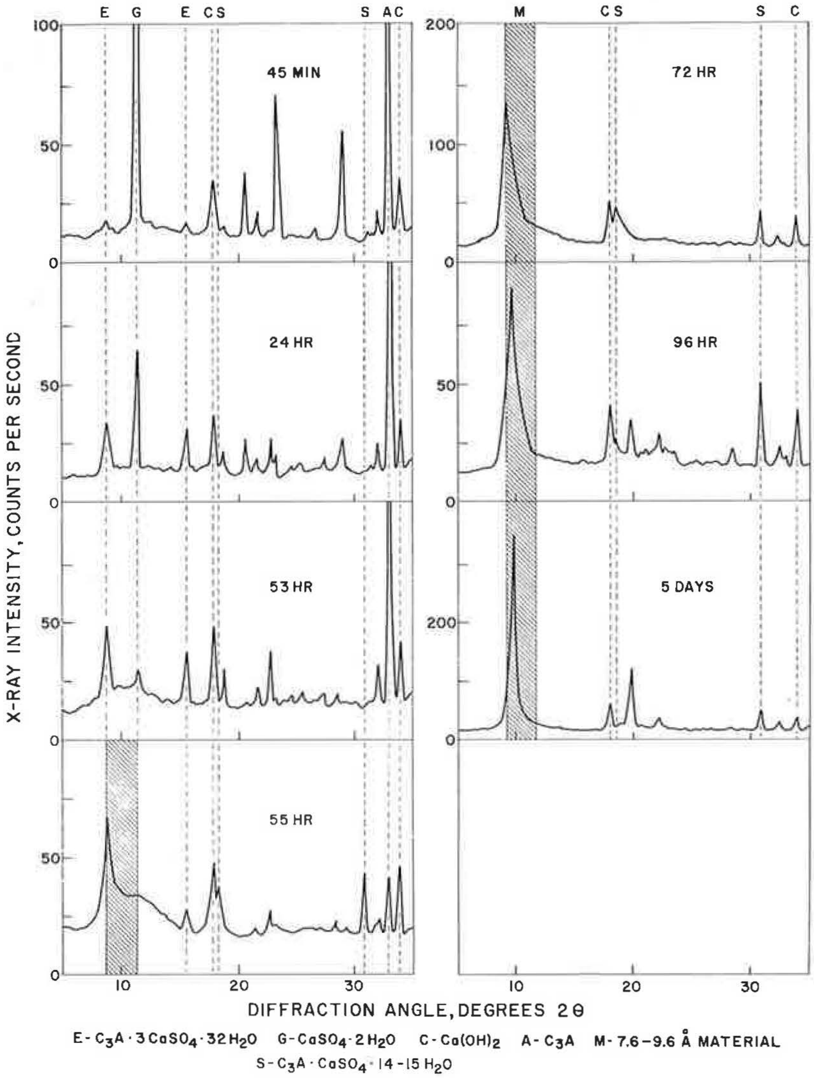

Figure 2. Diffraction patterns of base mixture with 3/4 mole SO_3 per mole alumina.

stage at which the gypsum has reached final depletion and a new set of reaction products shown more clearly in the 6-hr pattern is forming. The temperature rises noticeably at this stage. Peaks at 9.2° and 31.0° appear, indicating formation of the low-sulfate form of calcium sulfoaluminate hydrate, $C_3A \cdot CaSO_4 \cdot 14\text{-}15 H_2O$, by reaction of ettringite with more of the tricalcium aluminate. Turriziani (16) also has obtained evidence of this reaction. The intensity of the calcium hydroxide peak shows a slight decrease. Between 6 and 48 hr, the low-angle peak of the low-sulfate form of calcium sulfoaluminate hydrate continues to increase in intensity and to shift toward higher angles. The peak for calcium hydroxide continues to decrease in intensity. The low-sulfate form of calcium sulfoaluminate hydrate reacts with more C_3A and calcium hydroxide to form a solid solution. This reaction is accompanied by a decrease in intensity and the ultimate disappearance of the 31.0° peak. Earlier evidence for solid solution formation had been obtained by chemical analysis of the liquid phase (17). At 12 hr, a peak for C_4AH_{19} has appeared at 8.3° and continues to increase in intensity as the calcium hydroxide and tricalcium aluminate continue to react. At 48 hr, the C_3A has essentially hydrated completely. The final 48-hr pattern indicates that the C_4AH_{19} and the sulfate-hydroxide solid solution are essentially the only hydration products.

X-Ray Patterns of Complex Calcium Aluminate Salts

As indicated previously, complex solid solutions of varying composition and structure are formed during and after the later stages of hydration of the C_3A in the base mixtures. These hydration products introduce uncertainties into the stoichiometry of the reactions and also into interpretation of the X-ray patterns.

The situation is further complicated by the virtual impossibility of completely excluding carbon dioxide from the reaction mixtures. Carbonation is most intense at the surface exposed to the atmosphere, which is necessarily also the diffracting surface. As a result, marked distortion of the solid solution patterns is quite common, especially in samples subject to lengthy monitoring.

Under ordinary monitoring conditions sharp peaks, or broad bands with peaks, may be found anywhere in the angular range 9.2 to 11.8°, corresponding to a composition range

$$C_3A \cdot x\,Ca(OH)_2 \cdot y\,CaCO_3 \cdot (1 - x - y)\,CaSO_4 \cdot z\,H_2O \tag{1}$$

subject to the limitation that x + y cannot exceed unity. This angular range corresponds to a range of d spacing of 7.6 to 9.6 A. Because of the frequent uncertainty in composition and structure of the material exhibiting spacings in this range, the entire angular range is consistently presented here as a shaded area in the diffraction patterns of later hydration stages. The hydration product with spacings in this range will henceforth be termed 7.6 to 9.6 A material unless reference is made to identifiable specific phases. Table 1 lists known compounds in this range of composition, together with the angles or angular ranges in which they have been observed in studies of the base mixtures hydrated for various periods and at various temperatures. Examination of the second-order diffraction in an angular range at approximately double the diffrac-

TABLE 1

FIRST-ORDER DIFFRACTION PEAKS OF COMPLEX CALCIUM ALUMINATE HYDRATES[a]

Hydrate	x	y	Diffraction Angle, 2θ (deg)
Hydroxyaluminate	1	0	8.3
Monosulfate[b]			
form	0	0	9.8-10
$_1$form	0	0	9.1-9.3
$_2$form	0	0	8.5-8.7
Solid solution	0-0.4	0	9.8-10.1
Monocarbonate	0	1	11.6
Hemicarbonate	0.5	1 - x	10.5-10.9

[a] Of the form $C_3A \cdot x\,Ca(OH)_2 \cdot y\,CaCO_3 \cdot (1 - x\,y)\,CaSO_4 \cdot z\,H_2O$.

[b] Nomenclature of Turriziani (16).

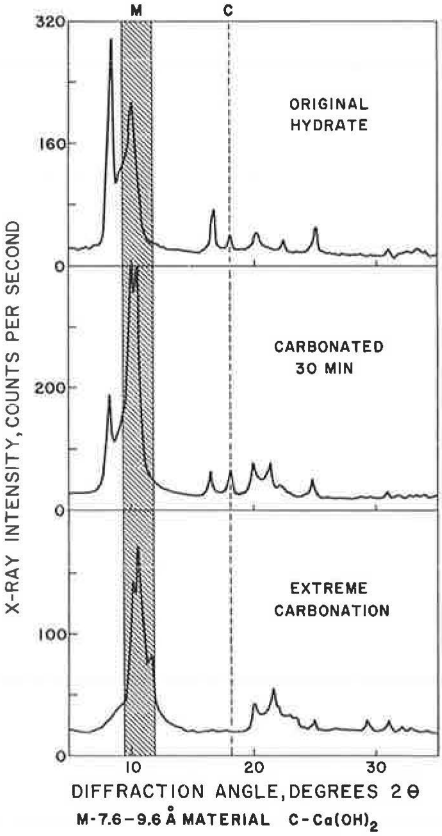

Figure 3. Changes in diffraction pattern of 7.6 to 9.6 A material caused by exposure of fully hydrated base mixture to atmospheric carbon dioxide.

tion angles discussed previously is sometimes useful in revealing the identity of the phases present.

The effect of carbonation is illustrated in Figure 3. Here the top pattern is that for the material before exposure and after 8 days of storage in a sealed container. The storage period has resulted in a recrystallization of the C_4AH_{19}, as reflected by the sharpening and narrowing of the 8.3° peak. The second pattern shows the effect of exposure to laboratory air for 30 min with the surface kept moist. The first-order peak for the hemicarboaluminate is clearly visible. The peak for C_4AH_{19} has decreased in intensity.

The bottom pattern in Figure 3 shows the effect of extreme carbonation of the material. The C_4AH_{19} in the original hydration product has been completely carbonated. The first-order lines for both hemi- and monocarbonate have appeared. The absence of any clearly defined new sulfate-containing material indicates that the calcium sulfate present remains in the 7.6 to 9.6 A material.

Numerous studies of equilibrium mixtures in the range covered in Formula 1 have only partially resolved the problem of identification of phases. The crystalline state of the monosulfate depends not only on temperature but also on previous history of the sample in a manner not yet understood. If calcium hydroxide enters the phase, the solid solution pattern is obtained uniquely. With sufficient lime, C_4AH_{19} and the solid solution can coexist, thus indicating some upper limit for x when y is zero in Formula 1. It might thus be expected, and has in fact been experimentally verified, that hydration of base mixtures containing high gypsum contents will not produce a sulfate-free phase. Base mixtures with a SO_3/Al_2O_3 mole ratio of about 0.7 or higher exhibit this behavior. This result corresponds to an upper limit of about 0.3 for x when y is zero in Formula 1. In the absence of CO_2, modified base mixtures, with calcium hydroxide contents adjusted to give $CaSO_4/Ca(OH)_2$ mole ratio a value of $(1 - x)/x$ in Formula 1, hydrate with complete consumption of calcium hydroxide. In sulfate-free compositions, the hemicarbonate can coexist with either C_4AH_{19} or with the monocarbonate in the appropriate composition ranges. The data indicate that the previously assumed (4) value of 0.5 for y when x is 1 - y in Formula 1 is essentially correct.

Stages of Hydration

Figure 1 indicates that the hydration of C_3A in a base mixture takes place in three stages. In stage I, the C_3A combines with the gypsum to form ettringite. Stage I terminates and the next stage of hydration begins when the gypsum is depleted. Stage II is characterized by reaction of the ettringite with more C_3A to produce the low-sulfate form of calcium sulfoaluminate hydrate and is terminated when the ettringite has completely reacted. Consumption of C_3A is much more rapid than in the first stage and is accompanied by considerable evolution of heat. During the last stage of hydration, stage III, the remaining C_3A reacts with calcium hydroxide and with the low-sulfate form of calcium sulfoaluminate hydrate to form 7.6 to 9.6 A material. The times of termination of these stages can be used as convenient qualitative measures of the average rates of the respective hydration reactions. Instantaneous reaction rates are difficult to ascertain quantitatively by measurements of diffraction line intensities in these systems because of the distortions of the specimen surface produced by volume changes and because of the preferred orientations produced by smoothing of the specimens.

Hydration at Moderate Gypsum Content

Figure 2 demonstrates essentially the same sequence of events as Figure 1, but at the slower rate expected from the higher gypsum content. The initial pattern at 45 min reflects the change in composition; the gypsum diffraction intensity is much higher and the C_3A diffraction intensity somewhat lower than at a correspondingly early hydration stage in Figure 1. The sequence of events and the reaction products are essentially the same as before and can be seen more clearly because of the lower rates and higher intensities. Stage I hydration is complete at 53 hr. The pattern at 55 hr shows that stage II is almost terminated; it actually terminated less than an hour later. Stage III terminated at 72 hr. The succeeding patterns show continuing recrystallization in the 9 to 10° range. No C_4AH_{19} was formed at this higher SO_3 content.

These descriptions demonstrate the feasibility of direct observation of the chemical reactions occurring in the hydration of the base mixtures and the techniques used for this purpose. Further studies have been made to determine the effects of various factors on the rates of hydration.

Effect of Water Content

Comparisons have been made of the hydration behavior of base mixtures at various water contents, even though slurries with high water contents cannot be monitored directly and require filtration. It was found that at least stage I hydration was accelerated by the presence of excess water. Significantly, in numerous experiments in which excess water was used, only the rates of reaction were affected. The chemical nature and the sequence of the reactions remained unchanged. These facts make it possible to study a particular stage of reaction by determination of the nature of the solid phase of a slurry by X-ray diffraction and the composition of the corresponding liquid phase by chemical analysis. The slurry must be filtered only when the desired degree of reaction has been attained. For study of various hydration stages of the same mixture, either filtration of duplicate mixtures at various times or successive sampling of a large quantity of slurry has proven equally satisfactory.

Effect of Fineness

Reference has already been made to the effect of fineness on the hydration characteristics of C_3A. Table 2 gives results for base mixtures made from various grinds of a particular batch of tricalcium aluminate at a SO_3/Al_2O_3 mole ratio of ¼. The results show that hydration rates at stage I and II increase with fineness.

Auxiliary Experiments

Two sets of experiments using other techniques have been made to assist in the understanding and application of the X-ray results.

Nature of the Hydrated Surface. —An indication of the texture and location of products of base mixture hydration has been obtained by an auxiliary experiment using sintered slabs of tricalcium aluminate, prepared as described earlier. In these studies, a C_3A slab was positioned ¼ in. from the surface of a slab of compacted powdered gypsum. In the first test, a pair of slabs was covered with a saturated solution of gypsum. Little if any visible change occurred on the C_3A slab. Diffraction revealed a thin layer of ettringite, formed at the surface of this slab and apparently sufficiently impermeable to prevent further reaction. In a second test, a pair of slabs was covered with a saturated calcium hydroxide solution. The hydration in this configuration was the same as in the first one. When a pair of slabs was covered with distilled water, a gel-like white layer formed rapidly on the C_3A surface and continued to thicken for 17 hr. X-ray diffraction revealed the presence of three layers, containing, successively, ettringite, the α_1 form of monosulfate, and finally, dicalcium aluminate octahydrate adjacent to the unhydrated C_3A.

The results obtained in these experiments are readily explained on the basis of the chemical reactions already observed in base mixtures. The following comments are numbered in the order of the slab pairs to which they apply:

1. If calcium sulfate is present in the original contact solution, a tightly adhering and relatively impermeable thin layer of ettringite is rapidly formed at the tricalcium aluminate surface.
2. The presence of calcium hydroxide initially in the absence of the sulfate is known to retard hydration (2). After the calcium sulfate entering the solution reaches the C_3A surface, the hydration process is similar to that in the gypsum solution.
3. In the absence of a retarder, the initial hydra-

TABLE 2

EFFECT OF PARTICLE SIZE OF TRICALCIUM ALUMINATE ON RATE OF HYDRATION OF BASE MIXTURE

Sample No.	C_3A Fineness (mesh)	Hydration Time (hr)	
		Stage I	Stage II
1	325-400	54	20
2	- 400	4.8	6.3
3	- 400*	1.0	1.4

*Sample 2 reground to a specific surface of 4,100 sq cm/g (Blaine).

tion reaction penetrates more deeply. Auxiliary experiments using the drying procedure described in the section on X-ray techniques have clearly verified that the initial reaction product in the absence of appreciable sulfate ion is a mixture of the hexagonal hydrates, C_2AH_8 and C_4AH_{19}. As the calcium sulfate from the gypsum slab reaches the surface, a layer of ettringite ultimately forms. The thinness of the ettringite layer indicates retardation of further reaction of the calcium sulfate in solution. This situation differs from the others in that the layer covers hydrated rather than unhydrated material and also in that the hydration continues. It must, therefore, be assumed that in this case the ettringite layer allows permeation of the liquid phase. Low mobility of the calcium sulfate through the ettringite layer results in further reaction of the C_3A surface with water to produce the di- and tetracalcium aluminate hydrates. The hydrated layer below the ettringite then provides a medium for formation of the low-sulfate calcium sulfoaluminate hydrate by migration of calcium sulfate out of the ettringite structure. Finally, the C_4AH_{19} combines with the monosulfate above it, leaving a layer of C_2AH_8. This reaction should produce a layer of solid solution immediately below the monosulfate. No such layer was observed, perhaps because it was thinner than the increment of grinding. Apparently sufficient sulfate ion is present in all layers to prevent formation of the cubic C_3AH_6.

These results throw light on the mechanisms of the reactions occurring in the hydration of the base mixtures. As long as the calcium sulfate concentration in solution is sufficiently high, only ettringite can form. When the depletion of gypsum causes a reduction in the calcium sulfate concentration, the calcium sulfate from the ettringite reacts with further unhydrated solid material and the ettringite decomposes to produce the low-sulfate form of calcium sulfoaluminate hydrate. The accompanying increase in rate of heat evolution indicates that the layer becomes more permeable as the ettringite reacts. When the ettringite is depleted, the calcium sulfate concentration in solution decreases to a point that permits calcium hydroxide and further C_3A to combine with the reaction product to form the solid solution.

Volume Changes During Water Imbibition. —The observed imbibition of water by base mixtures in the X-ray sample holder was investigated further by the osmotic cell dilatometers described earlier. Figure 4 gives observed expansions for a series of base mixtures with SO_3/Al_2O_3 mole ratios varying from $\frac{1}{8}$ to 1. The reported expansions are based on the initial volume of the reaction mixture as calculated from densities given by Lea (18, p. 227).

Calculation of the water requirement for the formation of ettringite during stage I hydration shows that the water-to-solids ratio of 0.4 in base mixtures provides sufficient water over the range of gypsum contents used. This conclusion is confirmed by results of base mixture hydration in the absence of a water reservoir. Stoppage of hydration by water deficiency occurs only after stage I hydration reaction has gone to completion. Only a slight expansion of the mass in the X-ray sample holder is observed.

The data show, on the other hand, that initial access to water results in large-scale imbibition and expansion even against the slight mercury pressure. This effect cannot be caused by the chemical requirement for water and must be associated with crystal growth. The expansion continues during stage II and III hydration and increases the water content to a level sufficient for completion of the later hydration reactions.

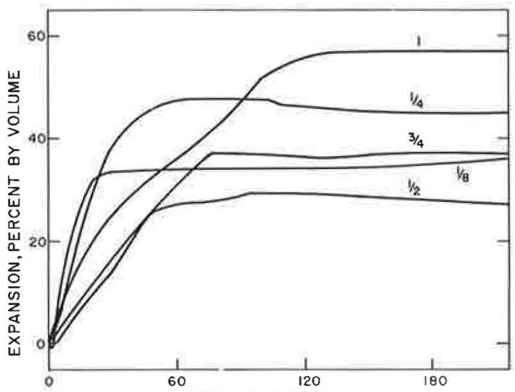

Figure 4. Volume increase from imbibition of water during base mixture hydration for varying SO_3/Al_2O_3 mole ratios.

Hydration at Lower Lime Contents

In the course of various exploratory and auxiliary studies, a considerable body of information has been obtained concerning the hydration reactions of mixtures of tricalcium aluminate, calcium hydroxide, and gypsum containing less than 1 mole of calcium hydroxide per mole of alumina. Although not directly applicable to cement hydration, the results obtained are necessary as background for portions of the present paper and are, therefore, given in the Appendix.

EARLY HYDRATION REACTIONS OF PORTLAND CEMENT

X-ray diffraction studies have previously been reported on aged hydrated cement pastes (19), predried and enriched pastes (16, 20), dried fresh pastes (21), and fresh pastes with an indeterminate moisture content (20). The published literature contains no reports of studies on fresh pastes deliberately maintained in a saturated condition.

Attempts to use the controlled atmosphere and temperature diffractometer for direct observation of the hydration of cement-water pastes met with numerous difficulties, as might be anticipated from earlier work (16). The most active ingredients at very early ages are present in such small quantity that identification of the hydration products is very difficult. The overlap of lines of the cement constituents is such that rates of hydration reactions cannot be readily estimated by observation of decreases in peak heights of individual compounds.

The present investigation is based on the observed similarity in hydration behavior between base mixtures and portland cement pastes, which indicates that the hydration reactions in the two systems are similar. It must be borne in mind, however, that the diffuseness of the diffraction patterns obtained from hydrated portland cement is definite evidence that the reaction products are structurally different from those of the base mixtures.

Comparison of Base Mixture and Cement Hydration

The sequence of chemical reactions in the base mixtures, leading first to a high-sulfate form and then to a low-sulfate form of calcium sulfoaluminate hydrate, is identical with the sequence that has been postulated for early cement hydration reactions. Transformation from high- to low-sulfate form of sulfoaluminate phase is generally agreed on (18, pp. 205-208; 22). Special mention must be made here of the work of Turriziani (16) who failed to find the low-sulfate form in fractionated pastes that had undergone considerable manipulation before examination with the result that the SO_3 and R_2O_3 were no longer together in the same fractions. He reports lines in the range 10.7° to 11°, which could be interpreted as calcium hemicarboaluminate hydrate resulting from carbonation, or possibly a dehydrated form of the low-sulfate form of calcium sulfoaluminate hydrate (17) which has been observed at spacings as low as the reported range.

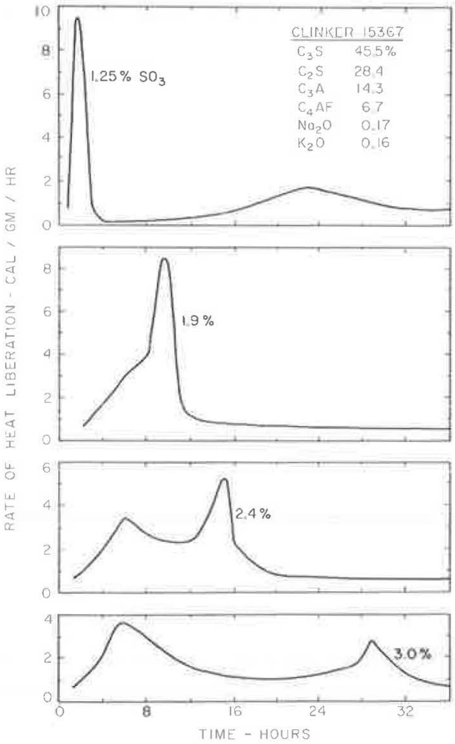

Figure 5. Increasing gypsum content delays final period of rapid cement hydration.

The phase equilibrium studies of Jones (22) had indicated the possibility of formation of solid solution. In addition, Steinour (23) had suggested the formation of a sulfate-free hydrate. The variations in gypsum content produce changes in reaction rate corresponding to the known retarding effect of gypsum on cement hydration. The effect of greater specific surface in accelerating the reactions also corresponds to well-known characteristics of cement hydration. In addition, the behavior of the sintered C_3A slabs corresponds precisely to a widely accepted mechanism for retardation of clinker hydration by gypsum which assumes an impermeable ettringite coating on the C_3A particles (24).

Further evidence of the similarity is provided by Figure 5 which has been reproduced from the earlier work of Lerch (2). These curves represent rates of heat evolution during hydration of a clinker ground with various quantities of gypsum to produce the indicated SO_3 contents. The initial heats of hydration are not shown in the figure; only the second and, where they exist, the third cycles of increasing reaction rate are shown. The effect of SO_3 content on the time of occurrence of the third cycle of increasing reaction rate in cement hydration can be unambiguously associated with the observed increases in duration of stage I hydration and the increases in rate of hydration of the base mixtures at the beginning of stage II.

The observed similarity between the hydration of the base mixtures and cement-water pastes can be readily explained on the basis that the calcium silicate phases of cement are relatively inert during the very early stages (25) and act only as sources of calcium hydroxide. The base mixtures thus contain most of the active components of fresh cement pastes.

It must be emphasized that the water-to-solids ratio of 0.4 used in the base mixtures provides considerably less water for hydration than is present in concrete at the earliest stages of hydration of cement. In the latter situation, all water present is available to the gypsum, C_3A, and ferrite phases because of the inertness of the calcium silicate phases. Thus, in a cement containing a total of 35 percent of the active components (C_3A + ferrite + gypsum), a water-cement ratio of 0.5 would yield a water-to-solids ratio of 1.43 for the active solids, until the rate of hydration of the C_3S becomes appreciable. The observed imbibition of water by the samples of base mixtures and the resulting expansion of the samples thus cannot be directly related to early volume changes in cement hydration or to the well-known expansion in water of cements with excess gypsum.

Studies on the effects of the other cement components on the hydration behavior of the base mixtures have led to further insight regarding the nature of the early cement hydration reactions. The results obtained on selected combinations of cement constituents have served to demonstrate clearly the role of tricalcium aluminate in the hydration of portland cement and to lay a foundation for the studies of the effects of admixtures and other applications.

Hydration of Ferrite Phase

Pastes have been monitored in which the C_3A of the base mixtures was partially or completely replaced by a ferrite phase. In these studies, the design of the mixtures was based on essentially the same principles that governed the design of the base mixtures. The existence had to be considered of a set of calcium ferrite and sulfoferrite hydrates completely analogous to the calcium aluminate and sulfoaluminate hydrates (16). Just as the $Ca(OH)_2$ content of the base mixtures was determined on the basis of possible formation of C_4AH_{19}, so the calcium hydroxide content should, theoretically, have been increased to give the mole ratio, $CaO/(Fe_2O_3 + Al_2O_3)$, a value of 4. It was found, however, that such a degree of dilution of the other reactants was not necessary; the rates of reaction encountered were so low that the theoretically required quantities of lime proved to be excessive for the observation periods used. The mole ratios actually used varied from 2.5 to 3.5.

Hydration Rates.—Studies were made on modified base mixtures in which the C_3A was replaced by the compositions C_2F, C_6AF_2, C_4AF, or C_6A_2F, thus covering both end members, C_2F and C_6A_2F, of the aluminoferrite solid solution series, as well as materials representative of those found in cements. In all instances, the hydration rates of the modified base mixtures proved to be relatively low, even when the $SO_3/(Al_2O_3 + Fe_2O_3)$ mole ratio was as low as $1/8$.

Further studies were made on these mixtures in slurries containing an excess of water and agitated continuously in plastic bottles on a rotating wheel. Although the excess water tends to speed hydration, the rates were still markedly lower than in the corresponding unmodified base mixtures.

In one test, a mixture of C_3A and a ferrite phase was tested. The molar composition was $\frac{2}{3}\,C_3A + \frac{1}{3}\,C_4AF + Ca(OH)_2 + \frac{1}{3}\,CaSO_4 \cdot 2\,H_2O$. After 17-days hydration in an excess of water, the diffraction pattern showed that considerable gypsum was still present and that stage II had not been initiated. Thus, not only did the ferrite hydrate much more slowly than the aluminate, but the presence of the ferrite phase actually retarded the normal stage I hydration reaction.

Hydration Products. —The hydration of mixtures containing the alumina-free phase, dicalcium ferrite, unlike that of the other mixtures, produced no observable reaction products even after 13-days hydration.

In all instances, the hydration behavior of the mixtures containing C_6AF_2, C_4AF, or C_6A_2F corresponded to the three stages of base mixture hydration, but at the lower rates already indicated. Diffraction patterns of these mixtures are indistinguishable from those obtained at a corresponding stage in base mixture hydration, except for stage III, where the absorption of calcium hydroxide is not accompanied by the usual changes in the pattern in the 7.6 to 9.6 A range. It has been established that the calcium ferrite hydrates have diffraction patterns almost identical with calcium aluminate hydrates (16). However, the presence of a red material in the hydrated mixtures in the present study indicates that some amorphous ferric hydroxide was formed. It has not been possible to determine at any particular stage the extent to which the observed crystalline hydrates contain ferric oxide as well as alumina. Over a period of weeks or months, the red color gradually fades. No change in diffraction pattern accompanies the color change. It is, therefore, reasonable to assume that the ferric hydroxide enters the crystalline phases present. However, with respect to ferrite hydration, the presence of the red ferric hydroxide indicates that simulation of cement hydration has not been as successful as in many other instances.

Effect of Alkalies

Previous work has shown that the alkalies are released rapidly (18, p. 478) during cement hydration. They must thus be added to the list of the active constituents present during the very early hydration. The known great chemical activity of these constituents would point to a considerable effect from their release.

Replacement of water by sodium or potassium hydroxide solutions in the base mixtures resulted in an acceleration of all reactions without any discernible change in the nature of the reaction products. However, in portland cement hydration the alkali release in not instantaneous, so that these observations cannot be considered necessarily representative of the actual situation.

To provide a closer simulation of cement hydration, base mixtures were made with sodium calcium aluminate in place of the C_3A. Under these conditions the alkali had a slight accelerating effect on the rates of reaction without any change in the reaction products. This can be seen by comparing samples 1 and 3 of Table 3 with the results already discussed in Figures 1 and 2. At a specific surface of 2,100 sq cm/g (Blaine), the alkali-containing samples in Table 3 hydrate at least as fast as the alkali-free samples of the figures at 3,100 sq cm/g (Blaine) at the same SO_3/Al_2O_3 mole ratios. The data in Table 3 also indicate the characteristic effect of changes in gypsum content.

TABLE 3

HYDRATION OF BASE MIXTURES WITH C_3A REPLACED BY SODIUM CALCIUM ALUMINATE[a]

Sample No.	SO_3/Al_2O_3 Mole Ratio	Hydration Time (hr)	
		Stage I	Stage II
1	0.25	2.5	0.8
2	0.50	18.5	8.5
3	0.75	55	7

[a] Sodium calcium aluminate with specific surface, 2,100 sq cm/g (Blaine).

An interesting result obtained with these mixtures containing sodium calcium aluminate has provided a basis for quantitative measurements. The mixtures were hydrated in an excess of water, and chemical analyses of the liquid phase were compared with X-ray

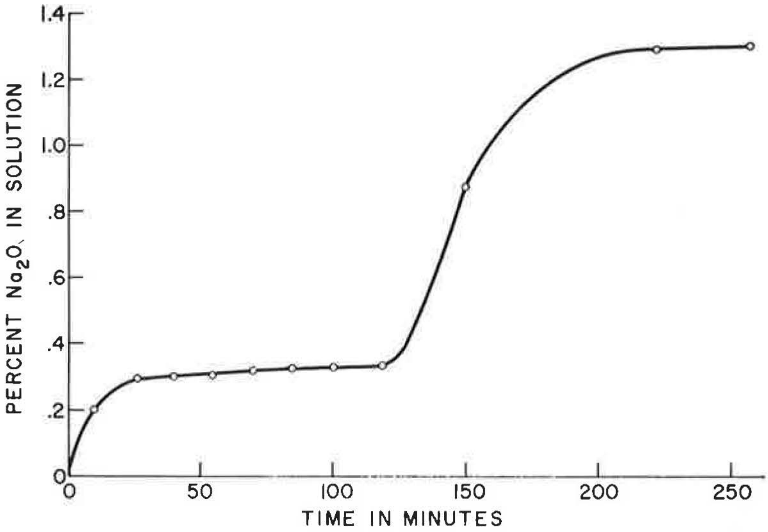

Figure 6 Release of Na_2O to liquid phase as quantitative measure of degree of hydration of sodium calcium aluminate.

patterns of the solid. The results indicated that the rate of release of the alkali into solution was equivalent to the rate of hydration of the aluminate phase itself. Figure 6 illustrates this phenomenon. In this particular instance the sodium calcium aluminate, calcium hydroxide, and gypsum were mixed in a mole ratio of 1:3:0.75. The water-to-solids ratio was about 6. The presence of the excess water allowed periodic withdrawals of the liquid phase for analysis. Stage I hydration is represented by an initial rapid release of alkali followed by a very slow release. Finally a very rapid reaction occurs, as indicated by the sharp rise in alkali concentration to a point indicative of complete hydration. This last stage of the reaction corresponds to stages II and III of base mixture hydration.

Attempts were made to use alkalies to increase the rate of ferrite hydration to a value comparable to that of C_3A in base mixtures. Slurry hydration tests of the various ferrites in mixtures with gypsum and calcium hydroxide in 3 percent sodium hydroxide solution demonstrated that the alkalies increased the hydration rate but not to the anticipated degree.

Effect of Tricalcium Silicate

Studies of the effect of tricalcium silicate on the reactions of the base mixtures demonstrated that the resulting hydration behavior more nearly approaches that of portland cement. In these studies the synthetic mixtures contained C_3S as a replacement for the calcium hydroxide of the base mixture.

Reaction Mixture Composition. —To determine compositions suitable for comparison with base mixtures, a study was made of the hydration stoichiometry of mixtures of various amounts of C_3S with tricalcium aluminate and gypsum in a mole ratio of SO_3/Al_2O_3 of 0.25. A water-to-solids ratio of 0.4 was again found adequate for maintenance of an adequate diffraction surface.

Free calcium hydroxide was observed in the final reaction product from these mixtures when the quantity of C_3S originally present was increased from 0.50 to 0.75 mole per mole of alumina. The Appendix describes similar tests in which calcium hydroxide was used. It can be seen in Figure 7 that a line, $g = 0.25$, intersects the boundary between regions B and C at $h = 0.75$. This means that when the mole ratio SO_3/Al_2O_3 is 0.25, formation of calcium hydroxide occurs only when the $Ca(OH)_2/Al_2O_3$ mole ratio is greater than 0.75. The experimental result indicates that C_3S releases 1.0 to 1.5

mole lime during early hydration and that suitable comparisons with base mixtures can be obtained by replacement of calcium hydroxide by at least 0.75 mole C_3S per mole $Ca(OH)_2$. In practice, an equimolar quantity was usually used.

Stage I Hydration. —Stage I hydration was somewhat accelerated when C_3S replaced calcium hydroxide in the base mixtures. This effect may be simply a result of the added water per unit C_3A during initial hydration or may also be an effect of the initial absence of calcium hydroxide. A physical setting (stiffening) resembling that of cement occurred during stage I hydration but did not affect the nature of the ettringite-producing hydration reaction.

Later Hydration. —The presence of tricalcium silicate produced marked changes in stages II and III hydration. The setting of the pastes restrained markedly the imbibition of water and the resulting expansion. There was a corresponding decrease in rates of reaction. Finally, it was found that the reaction products were relatively poorly crystallized.

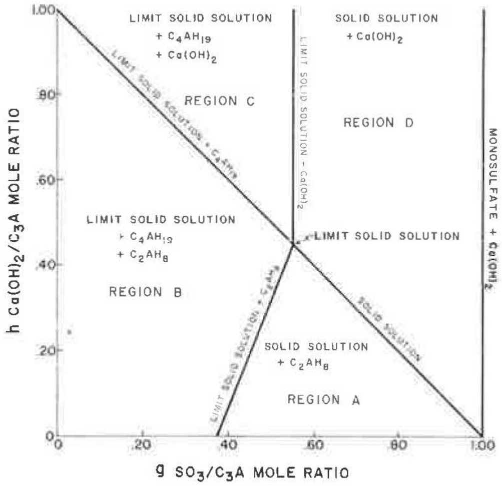

Figure 7. Nature of final hydration products of reaction mixtures containing C_3A varies with composition range. Final solid phases obtained from the hydration of C_3A depend on $Ca(OH)_2$ and gypsum content of reaction mixture.

Figure 8 shows the effects on reaction rates and products. Here a comparison is made between a base mixture and two pastes in which the calcium hydroxide of the base mixture was replaced by increasing amounts of C_3S. The patterns represent the hydration states at 24 hr. All three pastes became somewhat carbonated during the monitoring, but the essential features are clearly shown. In the interpretation of the patterns, consideration must be given to the lower C_3A and gypsum contents in the C_3S-containing compositions.

The retarding effect of C_3S on stage II hydration can be seen from the slight 15.7° ettringite line in the bottom pattern, which represents a paste in which 3 moles of C_3S replaced a mole of $Ca(OH)_2$. The relatively low intensities of the C_3A and $Ca(OH)_2$ lines in the top pattern, for the base mixture, indicate that stage III hydration is well under way. The middle pattern represents a stage III hydration condition less advanced than that for the top pattern, as shown particularly by the intense peak for the as-yet-unhydrated tricalcium aluminate.

Comparison of the patterns for the 7.6 to 9.6 A material in Figure 8 shows decreasing peak height and increasing line broadening as the C_3S content increases. This phase thus becomes progressively less well crystallized as the C_3S content increases and approaches the state occurring in cement. The effect is especially clear in the second-order diffractions at 20° to 23°.

For comparison, Figure 9 shows a pattern of a Type I cement containing 13.2 percent C_3A after 24-hr hydration. The essential features are seen to be present, even though the C_3A content is lower than in the bottom chart of Figure 8 and additional peaks for other anhydrous clinker components are present.

A closely related effect of the C_3S shown in Figure 8 is the absence of C_4AH_{19} in the hydration product from mixtures with low gypsum contents. Various auxiliary experiments in which both the gypsum and C_3S contents have been varied show that the excess of C_3A over that required for production of the 7.6 to 9.6 A material hydrates without producing a distinctive diffraction pattern. In the absence of gypsum, the effect shown in Figure 8 is accentuated to a point where no macrocrystalline material can be detected and it may be assumed that the hydration product enters the hydrous calcium silicate gel. This effect does not invalidate the reasoning on C_3S reaction mixture composition unless a mole of alumina carries more than 3 moles of lime into the gel.

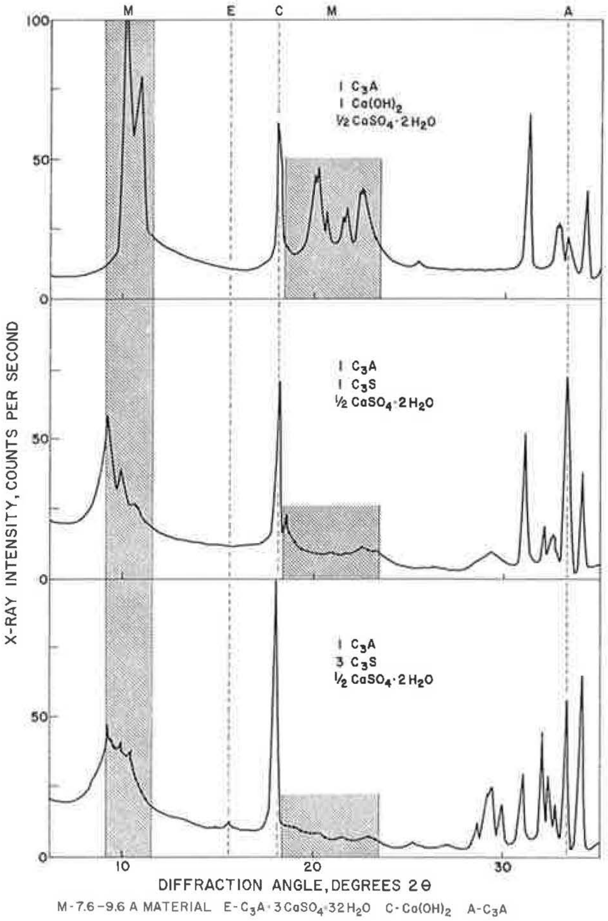

Figure 8. Replacement of calcium hydroxide by increasing amounts of C_3S retards hydration of base mixture and causes formation of poorly crystallized products.

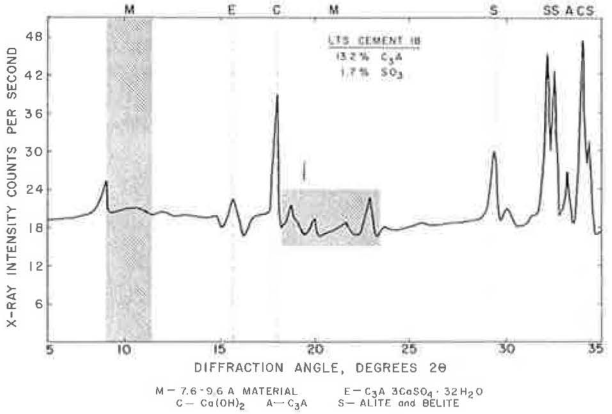

Figure 9. High C_3S Type I cement 24-hr diffraction pattern shows features illustrated in Figure 8 as modified by lower C_3A content and presence of additional clinker residues.

These results establish the relationship between the hydration behavior of portland cement and that of the base mixtures. They further provide an indication of the stoichiometry of early cement hydration reactions.

Volume Change. —The restraining effect of C_3S was investigated by use of the osmotic cell dilatometers. In this series of tests, the high C_3S contents used required a reduction of the water-to-solids ratio to 0.25 for formation of a paste of suitable consistency. The quantity of water per unit C_3A in the compositions is significantly greater than in base mixtures, so that smaller expansion was expected. For a mixture with 77 percent C_3S and a mole ratio SO_3/Al_2O_3 of $^1/_8$, Figure 10 shows that a relatively slight expansion occurred. Addition of gypsum to increase the mole ratio SO_3/Al_2O_3 to $^3/_4$ reduced the C_3S content to 71 percent and resulted in a significant expansion. For the same SO_3/Al_2O_3 ratio, addition of sufficient C_3S to raise its content to 83 percent produced the marked restraint shown. The expansion continues during the entire hydration process. Because the increase in C_3S content is accompanied by a corresponding decrease in C_3A, there appears to be some critical relationship between these quantities and the gypsum content which determines whether excessive expansions can occur.

Effect of Other Cement Constituents. —The effect of C_3S on hydration of base mixtures containing alkali is similar to that discussed previously. Further details of the behavior of this combination of materials will be considered in a later section on lignosulfonate admixtures.

In sulfate-free mixtures of C_3S and C_4AF, hydration of the ferrite phase retarded hydration of the C_3S. This result is a confirmation that the observed delay in C_3S hydration of undersulfated cements can be attributed to hydration of the ferrite phase (2).

Conclusions. —The early hydration of portland cement resembles closely the hydration behavior of base mixtures up to the time at which the cement sets. Setting, produced by hydration of the tricalcium silicate, retards further hydration of the tricalcium aluminate. The presence of the hydrous calcium silicate gel in hydrated cement causes a change in the stage III hydration reaction. The excess of C_3A over the quantity that can enter the sulfate-containing crystalline phase hydrates to become part of the gel rather than forming a crystalline C_4AH_{19} as in base mixture hydration.

EFFECTS OF CHEMICAL ADMIXTURES

The work described previously has yielded detailed information on the chemical reactions occurring in portland cement hydration during the period before setting and also on the role of tricalcium aluminate during the entire cement hydration process. The results obtained have been directly applied to clarification and solution of problems of practical interest arising from unusual hydration behavior of cement or from hydration under unusual conditions. Many of the applications provided additional confirmation of the conclusions already described and, in some instances, provided data that were used in arriving at these conclusions.

The present section deals specifically with the effects of chemical admixtures on the early chemical reactions and the interpretation of admixture activity in terms of the observed effects. Only relatively pure chemicals were used as additives in these initial studies to simplify interpretation. The techniques developed and the results obtained appear readily applicable to more complex situations.

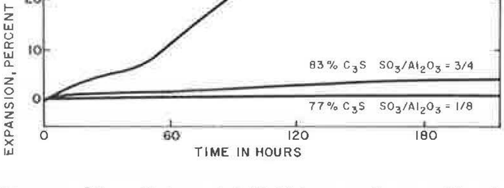

Figure 10. Water imbibition and resultant expansion at high C_3S contents.

Calcium Chloride

Though calcium chloride is known to form a complex hydrate with tricalcium aluminate, previous work (25) has indicated that this admixture has little effect on C_3A hydration reactions and that the observed acceleration of set and of strength development in cement paste or concrete results from an increase in the rate of

C_3S hydration. These results are supported by the present study. An addition of $CaCl_2 \cdot 2H_2O$ to a base mixture, in the amount of 10 percent by weight of C_3A and corresponding to a 1 percent addition to a cement containing 10 percent C_3A, produced only a slight retardation of the hydration reactions.

TABLE 4

EFFECT OF DELAYED ADDITION OF SUCROSE[a]

Sample No.	Additive (%)	Hydration Time (hr)	
		Stage I	Stage II
1	—	17	3
2	0.7	1.5	> 288
3	0.7[b]	60	>> 264

[a] Base mixture SO_3/Al_2O_3 mole ratio of 0.5, water-to-solids ratio of 2.0.

[b] Initially, 75 percent water added; sucrose dissolved in remainder of water and added after 1 min.

Sucrose

It is well known that sugar (sucrose) is an extremely effective retarder of the setting of portland cement pastes, although an initial rapid stiffening may occur (18, p. 253). The studies described here were undertaken primarily because of these properties and also because of the availability of the material as a pure chemical compound.

The initial effect observed in base mixtures containing sucrose was a very rapid acceleration of the reaction between the gypsum and the C_3A phase. A large ettringite peak was observed in the diffraction pattern at the earliest age of observation. Auxiliary studies established the reason for this behavior. The solid C_3A sorbs sucrose to produce a surface that does not permit the formation of the characteristically thin and relatively impermeable layer of ettringite. Thus, the reaction with gypsum could proceed to a greater degree before sufficient ettringite was produced to cause the usual retarding effect. No evidence of formation of unusual solid phases was observed. Further, the initial stiffening occurred in portland cement pastes containing sugar at very low water-cement ratios. Under these conditions the ettringite formed must act as a binder to stiffen the paste.

In demonstrating the effect of the sugar, it was found that one gram of C_3A could remove 99 percent of the sugar from 5 cc of 1 percent sucrose solution within 7 min. The presence of gypsum or calcium hydroxide did not interfere with this process. If C_3A was allowed to hydrate for a minute or two before the sugar was added, sorption was much less, whether gypsum was present or not. Thus, very early reaction of the C_3A surface with water altered the capacity of the surface for sugar. The effect of the immediate sorption on the nature of the ettringite coating was demonstrated by hydration studies of base mixtures; delayed addition of the sugar did not cause the initial rapid reaction (Table 4). After the immediate accelerated hydration reaction, the further reaction with gypsum in stage I when sugar was added initially was somewhat retarded and the subsequent reactions of stages II and III were greatly retarded. The decline in intensity of the C_3A pattern was exceedingly slow.

Subsequent experiments confirmed that the primary effect of sucrose in the hydration of cement is a great retardation of the rate of hydration of tricalcium silicate.

Lignosulfonate

Extensive studies have been made on lignosulfonate admixtures as an example of a widely used water-reducing and set-retarding admixture readily available free of other components that may be present in commercial formulations. Much information has been collected on the effects of lignosulfonates on hydration of the various cement components and on the effects of various cement components on the activities of the admixture.

Experiments on removal of a calcium lignosulfonate from solution show that C_3A rapidly sorbs considerable quantities, whereas C_3S and C_4AF sorb very little. Similar results have recently been reported by other investigators (26). It might thus be expected that the activities of sucrose and lignosulfonate would be very similar. This conclusion, however, proved to be false.

The incorporation of calcium lignosulfonate in base mixtures resulted in very little, if any, acceleration of the initial reaction between tricalcium aluminate and gypsum. Marked retardation of all hydration stages occurred, particularly in stages II and III. Figure 11 shows the effect on a system containing alkali, i.e., the effect of 3 percent sodium lignosulfonate, based on total solids, on the release of soda from the composition previously shown in Figure 6, the data from which are also shown for comparison. The effect of the admixture here is very similar to the retarding effect on base mixtures without alkali.

Studies with pats of C_3S and water revealed that additions of small quantities of eight different lignosulfonate admixtures could retard setting indefinitely, even though some of these contained appreciable quantities of $CaCl_2$. Diffraction patterns of these pats show no indication of calcium hydroxide formation. In the presence of alkalies, a delayed set ultimately occurs, and the effect of the admixture approaches that observed in cements. Apparently, the alkali reacts chemically with the admixture to destroy its hydration-inhibiting effect.

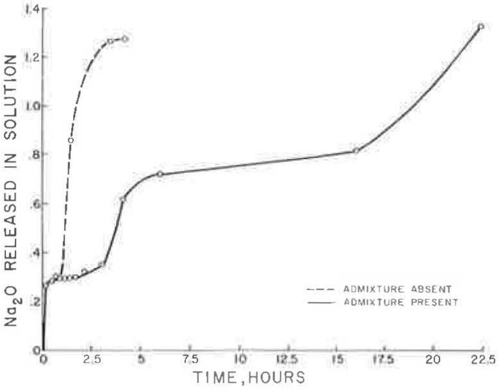

Figure 11. Delayed release of Na_2O to liquid phase showing retarding effect of lignosulfonate admixture on hydration of sodium calcium aluminate.

The behavior of lignosulfonates in more complex mixtures differs markedly from the effects on hydration of base mixtures or on C_3S alone. Table 5 gives the results of a series of tests in which sodium calcium aluminate replaced the C_3A in the base mixture to provide a source of alkali and to facilitate measurement of the degree of hydration by chemical analysis. The sodium lignosulfonate solution used is identical to "Admixture Solution QA" (27). Tests were carried out in the absence of a source of lime and also with $Ca(OH)_2$ or C_3S as lime sources. Excess water was used in these mixtures as in the tests shown in Figures 6 and 11. All mixtures contained sodium calcium aluminate and gypsum in a mole ratio of SO_3/Al_2O_3 of 0.5. The liquid phase, water or 0.5 percent sodium lignosulfonate solution, was added in a proportion of 5.8 ml/g sodium calcium aluminate. As a source of lime, 1 mole calcium hydroxide or C_3S per mole alumina was added. Samples of the liquid phase were analyzed after 10 min and after 17 hr of hydration.

Mixtures 1, 2 and 3 were control samples to show behavior in the absence of the admixture. Conclusions drawn earlier could be quantitatively confirmed in this series of tests. Comparison of mixtures 1 and 2 demonstrates the retarding effect of calcium hydroxide. Mixture 3 shows the early retarding effect of C_3S as a source of lime and the later retarding effect caused by the restraint of water imbibition resulting from the setting of C_3S.

The remaining mixtures in the table indicate that the effect of the admixture depends on a variety of factors, especially the ability of the admixture to inhibit the release of lime from C_3S and the effect of agitation. Comparison of mixtures 2 and 4 indicates the early retarding effect of the admixture and the marked retarding effect at longer hydration times. Substitution of tricalcium silicate for calcium hydroxide resulted in a very early acceleration of stage I hydration that could be further accelerated by agitation, as seen in mixtures 5 and 6. This behavior is very similar to the early effect of sucrose on hydration of base mixtures

TABLE 5

EFFECT OF LIGNOSULFONATE ON HYDRATION OF SYNTHETIC MIXTURES OF CEMENT COMPONENTS[a]

Mixture No.	Source of Lime	Admixture Present	Analysis of Liquid Phase (%)			
			At 10 Min.		At 17 Hr.	
			Na_2O	SO_3	Na_2O	SO_3
1	None	No	0.48	0.19	—	—
2	$Ca(OH)_2$	No	0.27	0.26	0.94	0.02
3	C_3S	No	0.27	0.34[b]	0.87	0.01
4	$Ca(OH)_2$	Yes	0.23	0.20	0.37	0.34
5	C_3S	Yes	0.38	0.46[b]	1.13	0.03
6[c]	C_3S	Yes	0.46	0.09	—	—
7	C_3S + 0.5 mole CaO	Yes	0.28	0.21	0.32	0.24

[a] Equimolar mixtures of sodium calcium aluminate and source of lime with enough gypsum to give SO_3/Al_2O_3 ratio of 0.5.
[b] Supersaturated with respect to gypsum (37).
[c] Mixture 6 agitated during first 10 min.

but apparently can occur here only in the virtual absence of calcium hydroxide in solution. The admixture inhibits release of calcium hydroxide from the tricalcium silicate; the highly alkaline solution decreases solubility of any $Ca(OH)_2$ present. Calorimetric data confirm that the observed behavior occurs also in cement, as indicated by significant increases in heats of immediate hydration when set-retarding admixtures are present. Mixture 7 indicates that inclusion of calcium oxide in the composition restores the retarded behavior of mixture 4.

The temperature of mixture 6 rose considerably during agitation. The sulfate content of the solution indicates that stage I hydration was completed in 10 min. Apparently, agitation caused exposure of fresh tricalcium aluminate surface to the liquid phase.

As indicated also in a recent report (28), delayed addition of the admixture resulted in decreased sorption with elimination of early acceleration. The resultant greater concentration of the admixture produced a greater retardation of all hydration stages than that produced by immediate addition.

APPLICATIONS

It is well known that changes in cement composition or the use of chemical admixtures can influence the properties of fresh mortar or concrete. Whereas many factors may contribute to these effects, there are a number of instances where a great similarity exists between the observed changes in concrete and corresponding changes in paste behavior. In these instances it can safely be assumed that the behavior of the cement paste is the primary factor.

False Set and Other Rheological Anomalies in Fresh Concrete

Results obtained in these studies have been especially useful in analyses of problems involving abnormal rheological behavior of fresh cement paste, mortar or concrete. Some applications to analysis are described in this section. These applications require primarily a knowledge of stage I hydration of C_3A because this stage of hydration continues throughout the period of interest for a normally retarded cement. Stage II hydration normally begins during or after setting.

The variations in the early hydration reactions encountered in specific applications depend not only on the content and activity of the C_3A in the cement, but also on the amount and state of the calcium sulfate. For clarity in the ensuing descriptions, a brief summary of existing information regarding the state and effect of the calcium sulfate during early cement hydration is first presented. For this purpose, the point of view of Gaskin and McGowan (29) has been adopted. The work at these Laboratories on false set (30) and related phenomena have led to the conclusion that, of all the points of view expressed in the literature, this one is outstanding in providing the most satisfactory explanation of the observed facts.

The state of calcium sulfate in a cement depends on both the time and temperature of grinding of the clinker with the gypsum. The resulting product in all cements is characterized not only by some degree of dehydration of the gypsum but also by some degree of disorganization of the crystal structure of any remaining fully hydrated gypsum. The disorganization, as well as the more commonly recognized dehydration, causes an increase in solubility. Thus, the early formation of a supersaturated solution of calcium sulfate is the rule, rather than the exception, during cement hydration.

The time of precipitation of well-crystallized gypsum from the supersaturated solution depends on availability or formation of well-crystallized gypsum crystals as nuclei. For low grinding temperatures and short grinding periods, the fragments of the original gypsum crystals cause sufficiently early precipitation, usually during the mixing of the concrete, and no interference with concrete placing operations occurs. With high grinding temperatures and long grinding periods, no suitable nuclei remain, and the delay in precipitation usually causes a plaster set (false set) after the mixing period.

This background will now be applied, in combination with the results of the X-ray study, to some problems of practical interest:

1. A particular high-capacity ready-mix plant using a 1-min mixing time in the central mixer experienced difficulty apparently caused by variations in cement. The cement usually produced normal concrete, but sometimes stiffened and produced cement balls that prevented proper discharge of concrete from the mixer. X-ray diffraction patterns revealed the gypsum in the "faulty" cement to be relatively well crystallized, whereas that in the "well-behaved" cement was thoroughly disorganized and highly dehydrated. Tests showed the latter cement to be, in fact, false setting, although not causing difficulty under the particular conditions of use. The observed difficulty with the "faulty" cement could thus be attributed to an early precipitation of gypsum at the end of the short mixing time. With the "well-behaved" false-setting cement, the gypsum precipitation occurred at a later time, while the concrete was in the truck mixers, and created no problem. This line of reasoning proved, indeed, to be true.

2. Various instances (31, 32, 33) have been reported of early stiffening of concretes containing normally setting cement when set-retarding and water-reducing admixtures have been used. The present studies indicate these effects to be attributable to two distinct causes, namely, acceleration of stage I hydration of C_3A and retardation of the precipitation of gypsum. Acceleration of stage I hydration can produce an early stiffening by increasing the quantity of hydration product, as was shown earlier to be an effect of sucrose; the resulting depletion of gypsum, in cements with relatively low SO_3/Al_2O_3 ratios, could cause a flash set. It might be expected that in instances of flash set this stiffening would not be reduced by further agitation and that an increase in sulfate content of the cement (31) would prevent the stiffening. Admixtures may also produce early stiffening by inducing false set. Auxiliary experiments in the present studies have shown that calcium lignosulfonate retards the setting of plaster. Thus, this admixture can, by delay of precipitation of gypsum, induce false set in an otherwise normally setting cement. This type of early stiffening can be reduced by further agitation, just as in other instances of false set. This retardation may be a factor in the reported variations in slump loss resulting from the use of chemical admixtures and may even contribute to plastic shrinkage cracking (34).

3. A case of anomalously slow setting concrete in a tunnel lining was recently described in the literature (27). This concrete, containing a lignosulfonate admixture, remained plastic for hours. The addition of gypsum to the cement resulted in a normally setting concrete. That report provided much of the impetus for the studies on alkalies described earlier. It was because of this interest that the tests reported in Table 5 were made with "Admixture Solution QA." From the results obtained in these studies as described in the following paragraphs, a complete explanation of the various observed effects could be obtained, and a major conclusion could be drawn that the observed excessive retardation resulted from a combination of factors and a chain of events that ultimately caused a lack of sufficient alkali release during the early hydration of the cement.

The cement used was a Type II, low alkali cement. Different shipments of this cement varied slightly in SO_3 content, but in all cases met specifications and exhibited normal setting behavior in the absence of the admixture. The excessive retardation occurred only when the admixture was used with cements of relatively low SO_3 content. Addition of gypsum to the cement restored normal behavior. For the excessively retarded cement-admixture combinations, a previous commentary (31) has noted the early consumption of C_3A, sulfate, and admixture, which the present studies show to be an adsorption of the admixture on the C_3A, accompanied by an acceleration of stage I hydration as demonstrated in Table 5. The observed rapid stiffening at 10 min in time-of-set tests and the relatively high initial Proctor needle penetration resistance for mortars containing the abnormally behaving combinations of materials point to an initially accelerated stage I hydration producing an early stiffening accentuated by low SO_3 content.

The remaining hydration of the cement can then be considered typical of an undersulfated, low C_3A, low alkali cement. Lerch (2) has shown that, in hydration of cements of this type, there is a high and very early heat release (as for flash set) followed by considerable delay in setting and in further appreciable rate of heat evolution. It is thus not surprising that an unusually long time of set would be observed in the present instance. However, Lerch's results did not indicate (2, Table 14) an extreme retardation of the type observed.

For an understanding of the extreme retarding effect of the admixture, the chemical composition of the cement must be considered. Chemical analysis showed the alkalies to be present as 0.47 percent soda and 0.03 percent potash. The release of soda, the major alkali, would be expected to follow a course such as that shown in Figure 10, where a considerable delay in alkali release during stage II is evident when a lignosulfonate admixture is present. C_3S will not set in the presence of a lignosulfonate unless some minimum quantity of alkali is present. The alkali level during the delay in stage II was probably too low to permit setting of the C_3S. Finally, this line of reasoning provides for the corrective action of additional gypsum. With added gypsum, stage I hydration is somewhat slower and consumes more of the aluminate phase, thus, releasing more alkali before the delayed stage II reaction is initiated. At a sufficiently high alkali level, normal setting of the cement during stage I hydration should occur, even in the presence of the admixture.

4. From the work done on sucrose, it was reasoned that sufficient acceleration of stage I hydration would prevent false set by an increase in the rate of removal of sulfate ion from solution. Because sucrose has no effect on the setting time of plaster (35), this conclusion could be investigated experimentally. Table 6 gives results obtained from the addition of sucrose to a false-setting cement. The results show that as little as 0.05 percent sucrose could prevent the premature stiffening of the paste. It was also found (Table 7) that sucrose was ineffective in preventing false set associated with aeration of the cement. If, as has been postulated, this aeration produces an inactivation of the C_3A surface, it can be concluded that sucrose is ineffective in reactivating the aerated surface.

"Optimum" SO_3 Content of Cement

Lerch's work was primarily directed toward evaluation of specification limits for SO_3 content of cement. Although the present studies provide a background for an understanding of many of the calorimetric results, progress has not yet reached the point where the observed effects on the ultimate properties of concrete can be understood. Some interesting conclusions can, however, be drawn from published results of the extraction test, ASTM Test Method C 265.

TABLE 6

EFFECT OF SUCROSE ON FALSE-SETTING CEMENT[a]

Sample No.	Sucrose (%)	Penetration (mm)					
		Init.	5 Min	8 Min	11 Min	15 Min	Remix
1	—	50 +	50 +	4	3	—	50 +
2	0.025	50 +	50 +	50 +	45	20[b]	50 +
3	0.05	50 +	50 +	50 +	50	45[b]	50 +
4	0.1	50 +	50 +	50 +	50 +	50 +	50 +

[a] Cement, Lot 19737, used with indicated quantity of sugar in ASTM Method C 359-56T.

[b] Because of possibility of a delayed false set, test was extended beyond time specified in test method.

TABLE 7

EFFECT OF SUCROSE ON AERATED FALSE-SETTING CEMENT[a]

Sample No.	Sucrose (%)	Pentration (mm)				
		Init.	5 Min	8 Min	11 Min	Remix
1	—	14	3	1	1	50 +
2	0.025	50 +	50 +	15	3	50 +
3	0.1	50 +	50 +	4	1	50 +

[a] Tests reported in Table 6 repeated after cement had been aerated for 24 hr at 74 F and 50 percent RH.

The marked decreases in sulfate ion concentration in the liquid phase occurring between 18 and 24 hr at the optimum gypsum content (36) must correspond to the termination of stage I hydration in that time interval. For pastes with gypsum contents at or below optimum, the X-ray and calorimetric evidence indicates that stage II and most of stage III hydration occur in 4 to 8 hr. Thus, the bulk of C_3A hydration at these gypsum contents occurs within approximately 32 hr. Under these conditions, very little expansive tendency remains during later hydration. About 32 hr is the latest age at which the paste structure can accommodate the expansive forces existing at the water contents used. The increased expansion in water at SO_3 contents higher than optimum can be attributed to continued hydration as indicated in the earlier discussion of Figure 10. This expansion may also account for the decrease in strength at higher SO_3 contents at later ages, but does not account for the optimum at 1 day.

Expanding Cements

It was pointed out earlier that the observed imbibition of water with resultant swelling of the base mixtures during stage I hydration could not be directly correlated with volume changes during portland cement hydration. It was also pointed out that in pastes containing sufficient tricalcium silicate, the expansive forces could be restrained. However, a large increase in the proportion of aluminate and sulfate phases, relative to the tricalcium silicate content, could well result in pastes which swell during hydration, as shown in Figure 10. This situation appears to be the basis of shrinkage-compensating or expanding cements. The various formulations studied for these materials have all depended on attainment of this effect by addition to portland cement clinker of admixtures containing calcium aluminates and calcium sulfate, or by blending such materials with portland cement.

SUMMARY AND CONCLUSIONS

X-ray diffraction studies of the reactions occurring in mixtures of tricalcium aluminate, calcium hydroxide, gypsum, and water have demonstrated that, for compositions corresponding to the sulfate-to-alumina ratios found in portland cements, tricalcium aluminate hydration takes place in three successive stages when excess lime is present:

I. Some of the tricalcium aluminate reacts with gypsum and water to produce the high-sulfate form of calcium sulfoaluminate hydrate (ettringite).

II. More of the tricalcium aluminate reacts with the high-sulfate form of calcium sulfoaluminate hydrate and with water to produce the low-sulfate form of calcium sulfoaluminate hydrate.

III. Still more of the tricalcium aluminate reacts with calcium hydroxide and the low-sulfate form of calcium sulfoaluminate hydrate to form a solid solution. The remainder of the tricalcium aluminate reacts with calcium hydroxide and water to form a tetracalcium aluminate hydrate, C_4AH_{19}.

The effects of the initial solid mixture composition and of fineness correspond very closely to the effects of these same factors during paste hydration of portland cement. Diffraction studies of sintered tricalcium aluminate slabs hydrated in various media have demonstrated the retarding effect of the initially formed ettringite film. X-ray and dilatometer studies have demonstrated that under conditions of access to water, hydrating C_3A pastes undergo large increases in volume because of a tendency to imbibe quantities of water far in excess of the stoichiometric requirements of the hydration reactions.

The individual effects of other portland cement constituents on these hydration reactions have been investigated. Partial or total replacement of C_3A by a ferrite phase, although introducing numerous experimental difficulties, appears to produce a series of analogous reactions in which Fe_2O_3 replaces Al_2O_3, occurring at a much slower rate. Addition of alkalies causes slight acceleration of the reactions. Replacement of calcium hydroxide by tricalcium silicate causes, as major effects, decreased crystallinity of the low-sulfate form of calcium sulfoaluminate hydrate and also absorption of excess C_3A by the hydrous calcium silicate gel, in place of formation of the sulfate-hydroxide solid solution. The setting of the C_3S causes retardation of hydration by providing restraint to the water imbibition observed when calcium hydroxide is used.

Study of hydration of combinations of the various constituents has led to a fairly complete picture of the early hydration reactions of portland cement and of the influence of various factors on these reactions.

The effects of a few well-known accelerating and retarding materials have been examined. In low concentrations, none of these materials affects the nature of the hydration reactions; only the rates are influenced. The effect of calcium chloride is almost exclusively an acceleration of C_3S hydration. Materials that cause retardation of set, such as sucrose or lignosulfonates, can also produce a large initial acceleration of the hydration reactions. This acceleration may be caused by inhibition of lime release by the silicate phases or by increased reactivity of the C_3A with gypsum, resulting from the very high sorption of the additive in the C_3A surface. The early acceleration and high sorption can be avoided by delayed addition of the retarder; the retarding effect is then markedly increased.

Careful consideration has been given to various cases of anomalous rheological behavior during early hydration. Recent results of X-ray diffraction studies of the state of calcium sulfate in cement are summarized. Short mixing times for concretes made from cements with little gypsum dehydration can result in stiffening at time of discharge from the mixer. Retardation of plaster hydration by an admixture can induce false set in an otherwise normally setting cement. Initial admixture-induced acceleration of hydration can lead, in effect, to undersulfating of the cement during later hydration. In high or moderate C_3A cements, a condition resembling flash set can then occur; in low C_3A, low SO_3 cements, abnormally long setting times may appear under these conditions. Lignosulfonates can retard the setting of C_3S indefinitely, but the effect is counteracted by the alkali released during hydration. In cements where the alkali is present predominantly as sodium calcium aluminate, admixture retardation of the hydration of this phase can result in abnormally low alkalinities which will cause marked increases in time of set.

Interpretation of earlier results obtained by ASTM C 265 indicates that the optimum gypsum content of a cement is that for which the formation of ettringite is complete between the ages of 18 and 24 hr. At higher gypsum contents, the moist-cured paste can no longer accommodate the expansive forces accompanying the reaction of ettringite formation so that higher expansions in water and lower strengths occur.

The observed water imbibition accompanying ettringite formation accounts for the behavior of shrinkage-compensating and expansive cements.

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Appendix

This Appendix contains a brief presentation of the final reaction products obtained in a variety of exploratory and auxiliary tests on relatively low-limed carbonate-free reaction mixtures containing C_3A and gypsum. Though the results obtained could be presented as a conventional phase diagram, the plot shown in Figure 7 is sufficient for present purposes. The abscissa, g, represents the SO_3/Al_2O_3 ratio and the ordinate, h, the $Ca(OH)_2/Al_2O_3$ ratio. The final hydration products in the four regions and along the four boundaries are shown. It has been assumed, for convenience, that the limiting solid solution contains 0.45 mole calcium hydroxide per mole alumina. This value actually may be as high as 0.5 or as low as 0.35.

The scheme shown is based in the following observations on hydration reactions:

1. The hydrate C_2AH_8 cannot coexist with $Ca(OH)_2$ but will react to produce C_4AH_{19};
2. The hydrate C_4AH_{19} cannot coexist with the monosulfate or with a low-limed solid solution but will react to produce a higher limed solid solution; and
3. The cubic phase, C_3AH_6, never forms in the presence of sulfate.

On this basis the hydration stoichiometry may be represented by the following equation:

$$\begin{aligned} C_3A + g\ CaSO_4 \cdot H_2O + h\ Ca(OH)_2 + w\ H_2O \rightarrow \\ a_1\ C_3A \cdot xCa(OH)_2 \cdot (1 - x)CaSO_4 \cdot zH_2O + a_2\,C_4AH_{19} + \\ a_3\,C_2AH_8 + a_4\,Ca(OH)_2 \end{aligned} \qquad (2)$$

in which the coefficients have the values shown in Table 8 for the various regions of Figure 7.

TABLE 8*

COEFFICIENTS FOR EQUATION 2

Coefficient	Region			
	A	B	C	D
a_1	$\frac{1}{2}(1 + g + h)$	$\frac{g}{1 - x_0}$	$\frac{g}{1 - x_0}$	1
x	$\frac{1 - g + h}{1 + g + h}$	x_0	x_0	$1 - g$
a_2	0	$\frac{1}{2}\left[1 + h - g\left(\frac{1 + x_0}{1 - x_0}\right)\right]$	$\frac{1 - g - x_0}{1 - x_0}$	0
a_3	$\frac{1}{2}(1 - g - h)$	$\frac{1}{2}(1 - g - h)$	0	0
a_4	0	0	$g + h - 1$	$g + h - 1$
w	$\frac{1}{2}\left[9 + z + (z - 9)h + (z - 13)g\right]$	$\frac{1}{2}\left[27 + 9h + g\left(\frac{z - 19 - 5x_0}{1 - x_0}\right)\right]$	$18 - g\left(\frac{20 - 2x_0 - z}{1 - x_0}\right)$	$z - 2g$

*x_0 is the upper limit of x.

A Study of Length Changes of Compacts of Portland Cement on Exposure to H_2O

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The various methods for studying the hydration rate of portland cement are reviewed, with particular reference to volumetric measurements. A new method is described for studying the interaction with H_2O of portland cement and its constituents by following the length change with time of a compact of unhydrated material; the formation and properties of the compacts are also outlined. The advantages of this method are discussed, the chief being that the particles of unhydrated cement are in direct contact with one another; this enables the length change to reflect immediately the formation of hydrated products at the particle boundaries and the study of hydration reaction and other effects within the first seconds of wetting. Sample size of the order of 1 by 0.25 by 0.06 in. allows close temperature control and the possibility of a study of vapor phase hydration is cited as a further advantage. Results of length changes are presented for vapor phase exposure at 20, 50 and 85 percent RH. Results are presented also for liquid phase hydration, including observations made only one minute after the start of hydration and including the effect of pre-exposure for periods from 5 min to 5 days at the three humidities on subsequent liquid phase hydration. The experiments showed that expansion begins immediately on exposure to water (liquid or vapor) and continues with time and that pre-exposure of the specimens even at low humidities has an effect on subsequent hydration rates. The meaning of "setting" and "hardening" with regard to compacts is discussed.

•THE HYDRATION rate of portland cement has been studied by many methods, one of these being the strength development of concrete as a function of time. Other methods include the microscopic examination of pastes and X-ray diffraction analysis of the unhydrated cement in hardened pastes. Whereas the latter method may eventually be best for measuring the rate of hydration of the individual phases, other techniques will always add to the knowledge concerning the mechanism of hydration. These techniques, listed as indirect methods (1), are concerned with the measurement of a change in the physical and chemical properties with time. Among these are the evolution of the heat of hydration, the change in the non-evaporable water, the development of specific surface, and the formation of calcium hydroxide. The volume change method, in addition to being a valuable adjunct to other methods, has some advantages because it reflects not only the chemical, but also the physical, changes.

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VOLUME CHANGE METHODS

When portland cement is in the presence of water, the chemical and physical changes that occur are accompanied by a reduction in the total absolute volume of the system. This was shown first by Le Chatelier (2) and later by Kuhl (3) and has also been shown for other hydrating systems (4). Le Chatelier also observed the apparent volume increase of the solid during hydration as made evident by the bursting of the inclosing vessels. A. H. White (5) reviewed the considerable experimental work (6, 7, 8, 9) done before 1915 on measuring the volume changes of neat cement and concrete bars. The results of this work showed that cement expanded continuously when kept in water and contracted markedly when maintained in air. This early work led to volume change studies which may be divided according to three methods:

1. Measurement of absolute volume change of the system by the dilatometer,
2. Measurement of apparent volume change of solids, and
3. Measurement of the sedimentation rate of paste and mortars.

Method 1 was refined by a succession of workers (2, 4, 10, 11) and was applied to plaster of paris, various types of portland cement, the effect of additives on portland cement, and gelatin. Although a good relationship between heat of hydration and volume decrease for portland cement was not obtained, a measure of the rate of hydration was found, including the effect of gypsum as the retarder.

Much of the work relating to Method 2 has been standardized (12) and applied to study of apparent volume change from the aspect of volume stability (13). In his investigations of varying compositions of free lime, magnesia, reactive silica in portland cement and various clinker compositions, Bogue (14) did, in effect, study the magnitude and rate of hydration of some of these components in cement. This volume change work extended into autoclave reactions, alkali reactivity of cement aggregates, and sulfate resistance of cements (15). More success in correlating volume change with reaction rate was obtained by L. Chassevent (11) for the plaster of paris system and recently in this laboratory for plaster of paris (16) and lime (17). Where the study dealt with a single chemical compound, the success was understandable as compared with multicomponent systems.

Method 3, used mainly by Powers (18) and Steinour (19), indicated that the size, shape, and number of cement particles are not altered appreciably by the reactions occurring within the first hour or so after contact with water. This method produced important physical evidence in opposition to the theory of Baikov (20) and Rehbinder (21) that at early hydration times, the cement particles are dispersed or "colloidized." As pointed out by Powers (22), the evidence on which the theory was based, the rapid development of area at early hydration times, may be explained by the thin layer of gel on the unhydrated cement particles.

In the development of the new volume change method, an attempt was made to overcome some of the chief limitations of the previous methods for measuring the apparent volume change, e.g., control of the temperature throughout the mass of the sample during hydration, and the ability to measure the length change from the moment the water comes in contact with the solid. This method affords the added feature of observing volume change when cement is hydrated with water in the vapor phase.

A NEW VOLUME CHANGE METHOD

It has been shown (23, 24) that dry, powdered, inorganic materials, such as calcium carbonate, silica, plaster of paris and calcium oxide (17), can be compacted to produce rigid porous bodies; further, these bodies can be used for the study of their length change isotherms. Compacts of unhydrated portland cement have now been produced and their length changes were measured during the period of hydration.

Materials

The cement used was a Type I with the chemical and physical properties shown in Table 1. It was obtained directly from the plant and stored in small sealed containers in desiccators over magnesium perchlorate. The extent of carbonation is indicated in Table 1.

TABLE 1

ANALYSES OF UNHYDRATED PORTLAND CEMENT

Analysis	Percent
Chemical:	
CaO	63.1
SiO_2	20.8
Al_2O_3	5.1
Fe_2O_3	3.5
MgO	1.5
SO_3	2.2
Na_2O	0.8
K_2O	0.7
Free lime	0.5
CO_2	0.14
Potential Mineralogical:	
C_3S	50.9
C_2S	21.4
C_3A	7.5
C_4AF	10.5
Physical:	
Blaine surface area	= 3,240 sq cm/gm
Autoclave expansion	= 0.01 percent
Initial set Vicat	= 3 hr 45 min
Initial set Gillmore	= 3 hr 30 min
Final set Gillmore	= 5 hr 15 min
Compressive strength:	
at 3 days	1,445 psi
at 7 days	2,617 psi

Experimental

Fabrication of Compacts. —The compacts were fabricated in a mold 1.25 in. in diameter, care being taken to insure that the material was evenly distributed so that the load could be evenly applied. Compacts were produced under pressures varying from 8,150 to 118,000 psi. The entire procedure was performed in a dry box using magnesium perchlorate (anhyrous) as a drying agent; it was found that the relative humidity in the box was maintained well below 1 percent. Sufficient material was compacted to give a final thickness of 0.06 in. and a specimen of rectangular shape, approximately 1 by 0.25 in., was cut from it. The sample normally weighed less than one gram.

Extensometer and Hydration Cell. —Because of the small sample size, an accurate means of length change measurement had to be used. This was achieved by a modified Tuckerman gage extensometer (Fig. 1). This optical instrument measured the length change with an accuracy of 2 × 10^{-6} in./in. The sample (1) was held against the knife edges (2 and 3) by a light spring (4), the sample resting on a holder (5). The optical system consisted of a fixed mirror (6) and a tilting mirror (7) which was one face of the rocking lozenge. The whole assembly was supported by a stand. The final assembly remained in the dry box during and after mounting of the sample on the extensometer and then was carefully placed in the hydration cell. This cell (Fig. 2) is made so that the sample can be subjected to high vacuum; ground glass joints and valves are used in its construction to exclude CO_2. The cell is provided with an optical window through which the extensometer can be read. A pipette arrangement is used for injecting water at a controlled rate when hydration in the liquid phase is to begin. Excess water may also be withdrawn from the sample when required.

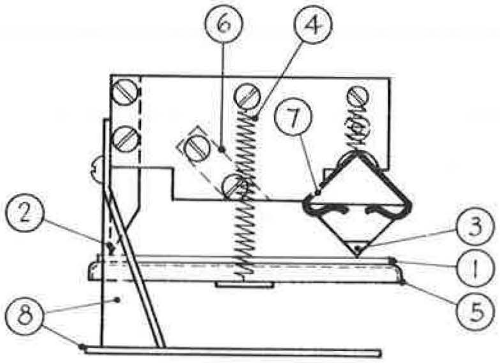

Figure 1. Extensometer.

When the sample and assembly are placed in the cell, the optical window assembly is placed on the ground joint (4) and the valve (2) is opened to vacuum (Fig. 2). After evacuation the cell is removed from the dry box and placed in a temperature controlled bath.

Measurement of Length Change as Function of Hydration Time. —The measurement of length change during the vapor phase exposure of the compact can be achieved at any desired humidity by joining the cell through the ball and socket joint to a vacuum system; from this system water vapor at any desired humidity may be obtained. Because this exposure proceeds with the exclusion of all gases except water vapor, the diffusion rate of the vapor is rapid and the desired humidity is attained quickly.

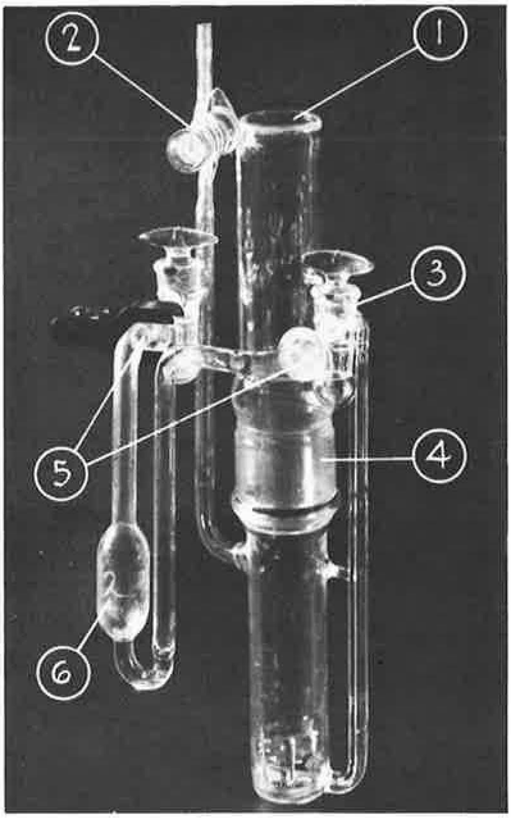

Figure 2. Hydration cell (1, optical window; 2, valve to vacuum; 3, controlling valve; 4, large ground glass joint; 5, ball and socket joint; 6, pipette).

Liquid phase hydration is also achieved without exposure of the sample to air. The pipette containing liquid water is placed on the joints (Fig. 2); the assembly is then placed in the constant temperature bath until the pipette has reached bath temperature. Water is then injected by the controlling valve (3) until the sample is entirely immersed. This procedure is completed in 15 sec, after which readings of length change begin. After a given time, the level of the water is lowered below the level of the sample by admitting some air into the cell.

Results

Mercury Porosimetry.—Plots of void fraction against the logarithm of the compaction pressure have yielded characteristic linear relationships for several materials (23, 25) and this is also observed for the unhydrated cement used in these ex-

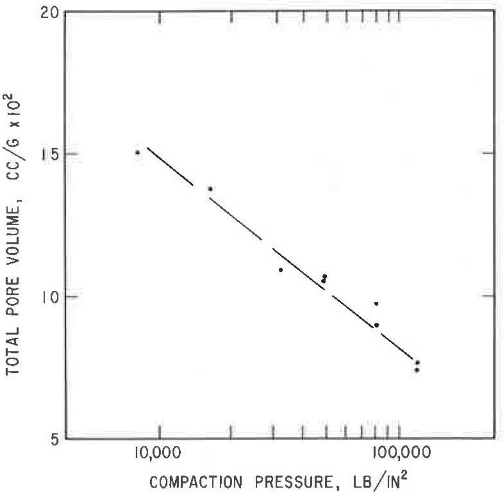

Figure 3. Relationship of total pore volume vs compaction pressure for unhydrated cement.

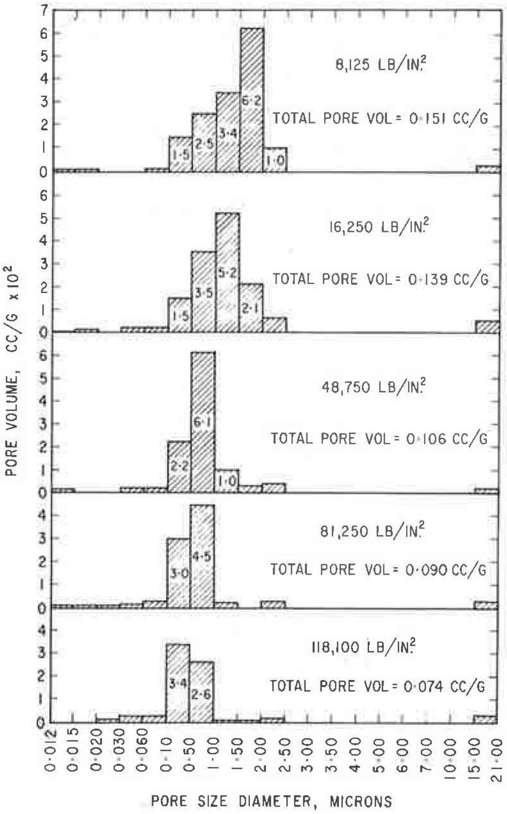

Figure 4. Effect of compaction pressure on pore size distribution and pore volume of unhydrated cement.

periments. Figure 3 is a plot of this relationship for compaction pressures varying from 8,150 to 118,000 psi. Mercury penetration results shown in Figure 4 illustrate how the pore size distribution is changed and the pore volume is lowered with increasing pressure of compaction.

Vapor Phase Exposure. —After initial degassing, during which only slight contraction was observed, vapor phase measurements were taken at three relative humidities: 85, 50, and 20 percent on compacts formed at 49,000 psi. Although readings were taken after 1 min, it was observed that an expansion began on exposure of the sample to water vapor.

For each humidity, the high initial rate of expansion was followed by a continually decreasing rate reaching a negligible value after 5 days, when the experiments were terminated. The higher the humidity, the greater was the initial rate of expansion and the final value for the expansion. The curves in Figure 5 are the mean values obtained from 10 to 30 experiments showing the general characteristics. Results varied somewhat depending on the bottle of unhydrated cement used even though from the same batch; deviation from the mean at each humidity was as much as 20 percent. It was observed, however, that expansions attained mean values of approximately 0.14, 0.08, and 0.05 percent after exposure to 85, 50, and 20 percent RH, respectively. The reproducibility is thus good enough to make the differences at the various humidities significant.

Liquid Phase Hydration. —Results were obtained for the expansion of the compacted specimen as a function of time from the first minute after they were submerged in water at 70 F. These results and those for samples subjected to pre-exposure to water vapor are included in Figures 6, 7 and 8. Although the expansion rate decreased with time, a measurable rate was observed for as long as measurements were taken (12 days). Expansion of up to 0.30 percent was obtained within a 24-hr period.

Effect of Vapor Exposure on Expansion Due to Liquid Phase Hydration. —Results showing the effect of pre-exposure at 85, 50, and 20 percent RH for times of approximately 5 min, 6 hr, 24 hr and 5 days are shown in Figures 6, 7, and 8. Rates are very much reduced for the 85 percent humidity curves and for the 5-day exposure the rate of expansion is almost negligible. Even for the 5-min exposure the rate was considerably reduced, indicating considerable interaction at so short a time. At 50 percent RH, results still indicate a considerable interaction, although to a much less extent than at 85 percent; exposure for 5 min at 85 percent will reduce the initial rate (length change for

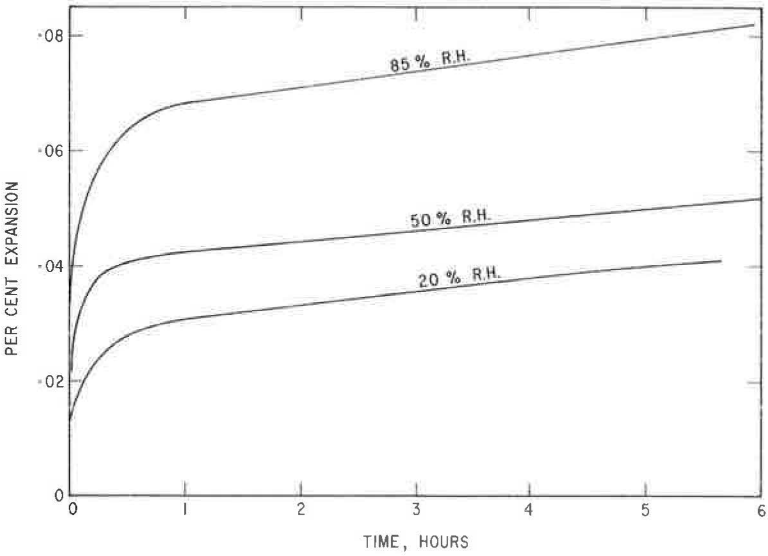

Figure 5. Expansion during exposure to various humidities.

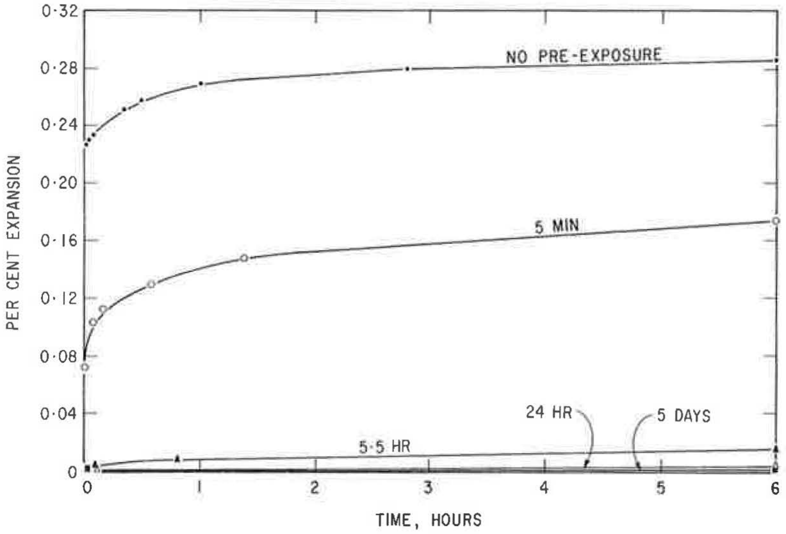

Figure 6. Expansion during submersion of cement pre-exposed to 85 percent RH for various time intervals.

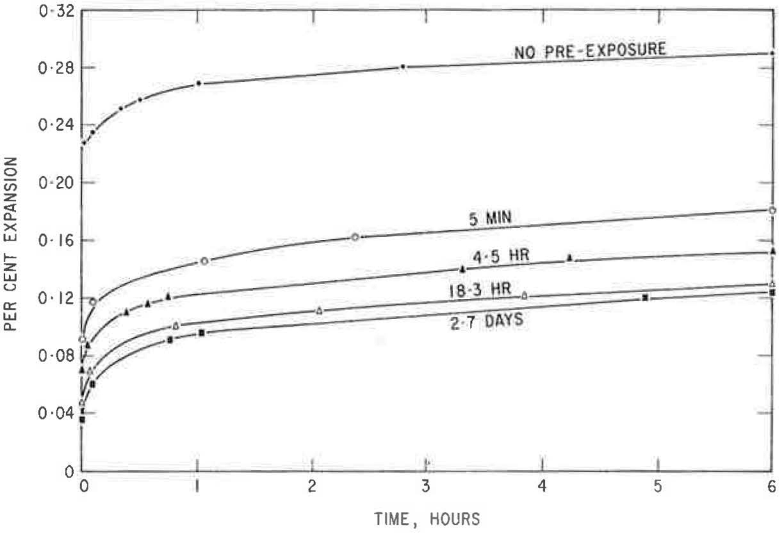

Figure 7. Expansion during submersion of cement pre-exposed to 50 percent RH for various time intervals.

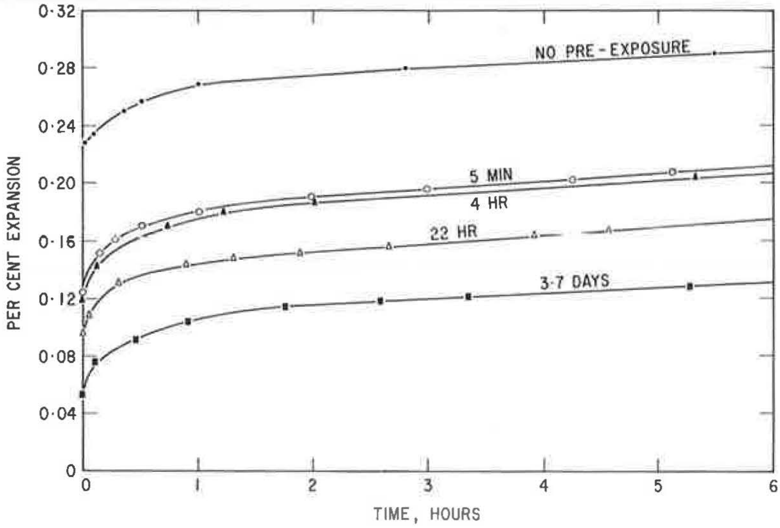

Figure 8. Expansion during submersion of cement pre-exposed to 20 percent RH for various time intervals.

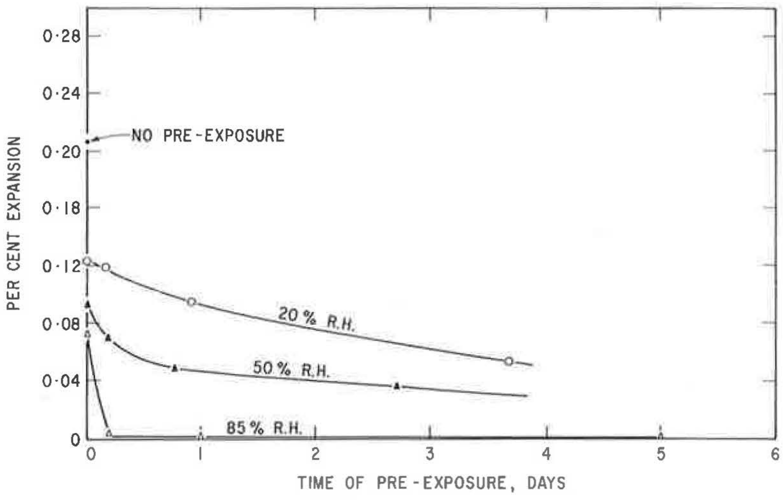

Figure 9. Expansion after first minute of submersion vs pre-exposure time to various relative humidities.

the first minute) as much as at 50 percent for 5 hr (Fig. 9). Continued exposure at 50 percent for greater than 5 hr does not greatly alter the initial rate of expansion. This is also indicated by the results of the vapor phase hydration (Fig. 5). Results of exposure at 20 percent RH show a similar trend. It is significant, as shown by the vapor phase results, that there is considerable interaction at such low humidities between the water vapor and the unhydrated cement.

The results obtained from submerging samples in water are reproducible for the samples that were pre-exposed for 5 hr, 24 hr, and 5 days at 85 percent RH. For the samples pre-exposed for 5 hr at 50 percent RH, the value of the expansion at 1 min may vary by 15 percent, whereas those pre-exposed at the same time at 20 percent humidity may vary by about 30 percent. If, however, samples were taken for which the results for vapor hydration did not vary more than 10 percent, the reproducibility of results of liquid phase hydration was within 10 percent. Although the cement may be affected to different degrees by the moisture and CO_2 contamination, the possibility of a variation of the clinker composition from sample to sample is very real. This is a disadvantage in using small samples. Despite these difficulties, the trends shown are considered to be significant.

Discussion

Pore Structure of Compact. —It has been shown (26) that the compaction behavior of powders depends markedly on their hardness and that their results are described by two nearly independent probabilistic processes. The first is the filling of holes of the same order of size as the original particles. This occurs primarily by particles sliding past one another, which may require slight fracturing. The second process is associated with the filling of voids substantially smaller than the original particles by plastic flow or by fragmentation. This process, however, does not add significantly to the surface area of the material (25). The pore structure of the compact is quite reproducible and, as shown in Figures 3 and 4, may be defined by the compaction pressure. The strength and rigidity of this body is probably derived more from physical than chemical forces, and as shown by Czernin (27), compacted bodies can develop fair strengths.

The compact, with its particles in direct contact and its natural rigidity, possesses the primary structure from which the final structure is developed on hydration (28, 29). The important characteristic is that it possesses this structure before any contact with water, and the effective water/cement ratio will be defined by pore volume of the compact.

Control of Conditions. —Because of their size, these bodies can be made in controlled humidity conditions and experiments can be performed in vacuum. Temperature control can be easily maintained externally but it is within a sample that control is difficult. The hydration of cement is an exothermic reaction and unless the heat can be removed rapidly from the site of the reaction, the temperature will rise. The likelihood of this happening depends on the mass of the sample for the quantity of heat liberated and on the thickness of the sample for the rate of heat transfer from within. Optimum conditions are achieved in this method by having a very thin sample; this is not usually possible in any of the other volume change methods.

The use of small samples also has the advantage of avoiding gradients of stress. When using large bars in the test, although of greater practical importance, the volume changes would not correctly reflect the progress of a reaction. Volume change gradients through the larger body can cause decrease in strength, and finally, destruction of the body.

Measurements at Early Times. —The primary advantage of this method is the ability to observe within the first minute the volume change when water comes in contact with the unhydrated cement particles. The sample is under vacuum when water is injected and this fosters the rapid distribution of water in the pores and consequent rapid wetting of all the surface. Because the particles are in contact with each other, any physical changes in the particles due to reaction will be reflected as an apparent volume change of the system. For these reasons the measurement of length change of a compact should reflect the rate of reaction without any lag in time.

Cement paste, as is used in the other volume change methods, is formed during several minutes of mixing and handling; it is a plastic cohesive mass composed of an aqueous solution and particles of clinker. Owing to the nature of the paste, molding techniques were used and sometimes, in the mortar bar methods, readings were not taken till 24 hr after the initial wetting. In other methods, however, readings were taken after 15 min or less; in the sedimentation technique, the time may be less.

The primary structure of cement paste is the network of discrete particles formed by the process of mixing the particles with water. These particles are separated from each other by water and until they come into contact with each other, an expansion due to initial formation of hydrate product on the surface of the particle cannot be observed. In fact, it has been reported (29) that the earliest time at which an expansion has been observed in portland cement paste is 1½ hr after mixing. Measurements in air of volume changes of normally mixed pastes have shown marked and extended contractions from early ages. Thus, no volume change representing the formation and movement of the hydrated product from the first instant of wetting can be made by other methods for liquid phase hydration.

Vapor Phase Exposure. —Measurement of volume change during vapor exposure can only be made by this method. The cement particles must never come into contact with water before the study, and the primary structure must not only be established but must be represented by particle contact so that the limited hydration which may take place can be detected and measured. This direct contact of the cement particles avoids all contraction during vapor phase exposure even at low humidities.

The discussion of primary structure and particle-to-particle contact leads to the subject of the "setting" or "hardening" of cement. As was pointed out by Steinour (30), these terms arose from practical considerations and are not theoretical. Nevertheless, there has been some debate as to the difference in the nature of the hydration process before and after setting. When the terms are applied to the hydration of compacted portland cement, one is forced to conclude that setting has taken place before hydration has begun or at least within a few minutes after exposure to water.

Study of Effect of External Agents or Additives. —The effect of retarders or accelerators on early hydration can be followed by volume changes in a similar manner as by the other methods: either by mixing the additive with the unhydrated cement powder or by dissolving it in the water to be introduced to the sample.

Greater versatility is obtained in this method, however, in the study of external agents. Effect of carbonation from the gas phase can be studied during vapor phase exposure with confidence of attaining uniform carbonation throughout the sample.

Interpretation of Results. —The initial expansion of the unhydrated cement compact may be attributed to the phenomena of stress relaxation, dispersion on wetting, physical adsorption, and hydration of the cement particles. In can be expected that dry powders when compacted should be found in a state of stress and that this stress may be relaxed through irreversible expansion when the body is wetted by liquids. Cyclic wetting by organic liquids, such as methanol, for similar systems did not result in irreversible expansion, thus indicating that the residual stress is negligible for the pressure ranges used in these experiments.

Compacts of some materials disperse when immersed in water. Such compacts, however, will behave as rigid bodies up to high humidities as was shown (23, 24) for compacts of calcium carbonate. For plaster of paris it has been found (16) that a small amount of hydration on the particles by exposure to vapor will prevent any disintegration on submersion in water. Compacts of unhydrated cement, even without exposure to vapor, show no tendency to disperse when immersed in water.

There is no doubt that some expansion will occur due to physical adsorption; at 20 percent RH, expansion may be due entirely to this, because some previous work (31) has suggested from measurements of "evaporable and non-evaporable water" that no interaction other than physical adsorption takes place at this humidity. The concept of "evaporable water," however, is somewhat arbitrary as far as an absolute definition of physically or chemically sorbed water is concerned. The amount of reaction product formed at 20 percent RH in all likelihood would be very small and may not be of the same nature as in liquid phase hydration; some form of chemisorption may be occurring. The formation of small quantities of hydration product formed on the surface of each particle may be sufficient to be detected by this technique.

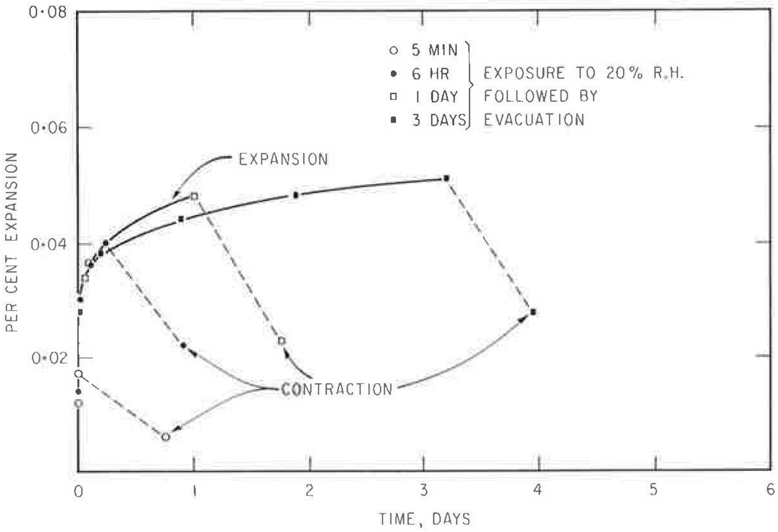

Figure 10. Expansion on exposure to 20 percent RH and contraction on evacuation.

The evidence for considering that chemical interaction takes place at 20 percent RH is:

1. Expansion occurred continuously, although at a decreasing rate for as long as observations were taken (5 days); this is illustrated in Figures 5 and 10 and presented in the results; for physical adsorption at low humidities, equilibrium is attained in a few hours.
2. Vapor phase exposure affects subsequent liquid phase exposure (Fig. 9); this must be attributed to chemical reaction because physical adsorption could not have this influence and water vapor pre-exposure was carried out in a high vacuum apparatus where CO_2 effects would be eliminated.
3. Expansion due to physical adsorption was observed (23) on compacts of various materials including precipitated calcium carbonate of particle size 2 to 5 μ; expansion at equilibrium when exposed to 20 percent RH was 0.018 percent. The particle-size distribution of the unhydrated cement, although varying between 1 to 50 μ, is such that the majority of the particles is about 10 μ. Physical adsorption could not be expected to produce a large expansion under these conditions but if a small quantity of hydrate product was already formed on the particles, a significant expansion would be expected. If this is the case, however, the sample must possess adsorbed water in equilibrium with the humidity where hydration can no longer occur (30 percent RH) and this sample on evacuation should produce contractions greater than those observed on subsequent exposure to 20 percent RH. On evacuation before exposure, contraction was in the order of 0.002 percent.
4. Results obtained by exposing four different samples to 20 percent RH for 5 min, 6 hr, 1 day, and $3\frac{1}{4}$ days, respectively, are shown in Figure 10. These samples were evacuated at high vacuum until no further contraction occurred. The time required for this was usually 24 hr. It is observed that after evacuation the sample remained substantially longer than the original length. The irreversible portion increased with time of exposure. This is consistent with the assumption that some chemical interaction is taking place during exposure to 20 percent RH, producing a high surface area product, the formation of which causes an irreversible expansion. As more high surface area product is formed, however, more contraction should occur on drying due to its higher surface area. If this effect was due to physical adsorption, the expansion should be reversible for all exposure times.

The concept of hydration occuring at low humidities is not new. Calcium oxide has been shown to hydrate completely at humidities as low as 20 percent (17, 32) and the presence of a "liquid phase" has been considered unnecessary due to the possibilities of "direct" or "solid-state" mechanisms. Several authors (33, 34, 35) have discussed the possibility of this mechanism and even at 50 percent RH this may be operative because capillary water would not exist at this humidity: the samples were evacuated before exposure and, thus, are on the "adsorption" part of the isotherm.

A portion of the expansion taking place on exposure of the unhydrated cement compacts to vapor is thus considered to be due to hydration. The vapor interacts with the unhydrated cement particles on the external surface, causing a pressure on the next particle due to growth of the hydrate product outward. Hydration may also take place within small cracks in the individual particles, causing each particle to expand individually; this may more easily explain the immediate expansion of the particles on exposure to vapor.

The initial expansion occurring on submersion of the compact in water may be due to both hydration and partial relaxation of the compacts. The hydration that is presumed to take place on vapor phase exposure even at 20 percent humidity, however, and the effect of reduction of the expansion rate on subsequent submersion indicates that the hydration product surrounds the particles with rapid setting of the cement taking place even in the vapor phase. The fairly high rate of expansion for the first minute even on vapor phase exposure leads to an expectation of a high expansion rate for the submersion experiments. It is concluded that the high expansion in the first minute of submersion even for samples without pre-exposure to vapor is due predominantly to hydration from the surface of the particles. This rapid initial expansion may be correlated to the rapid heat evolution that has been observed during the first few minutes of the hydration of cement (36).

The fact that hydration appears to proceed even at low relative humidity but at a decreasing rate with time indicates that products form an effective layer around the unhydrated material. At a higher humidity, the hydration may proceed further. This behavior differs from that of calcium oxide which hydrates completely in the vapor phase, though at a lower rate than in the liquid phase. This occurs even at relative humidities below 20 percent (17).

In the liquid phase, the rapid initial expansion, with decreasing rate, does not explain the dormant period and reacceleration observed by calorimetric measurements during early hydration (36). The fact that the effective water/cement ratio of the compact is approximately 0.10 may provide an explanation. Cement is a complex mixture of different compounds, however, and not until the behavior of each of them can be studied by this method can any interpretations involving the mechanism of hydration and the method of transport of the hydration product be made.

CONCLUSIONS

1. This method provides a means for following both by vapor and liquid phase the immediate formation of hydrated product at the surfaces of cement particles. Owing to the small size of the samples, control of conditions may be exercised.
2. Cement compacts appear to hydrate and expand immediately when exposed to relative humidities as low as 20 percent. No contractions are observed on vapor phase hydration of cement compacts.
3. Pre-exposure to water vapor has a considerable retarding effect on subsequent liquid phase hydration and this effect is a function of both relative humidity and exposure time.
4. Expansion due to liquid phase hydration of compacts begins immediately on wetting and continues at a decreasing rate for at least 12 days.

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A Durability Test for Aggregates

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The routine tests used in California to control the quality of aggregates, particularly bases and subbases, are grading, specific gravity, unit weight, absorption, soundness, Los Angeles rattler, R-value, cleanness and sand equivalent. A new test in which aggregates are degraded in the laboratory has been developed to measure the mechanical durability of aggregates in terms of a "durability index." The test was developed largely as a result of the need for a measure of the breakdown occurring to aggregates during construction and normal use under traffic conditions. Equipment and procedures used in performing the test are for the most part those used in the sand equivalent and cleanness value tests.

Test values on many aggregates from the coast ranges of California, which are abundant in sandstone, serpentine and shale, are low. However, the aggregates from Southern California show consistently high durability indices. There is little or no correlation between the Los Angeles rattler and the durability index for the majority of materials tested. This is not surprising because the two tests measure the results of different abrasion processes. Results of the durability tests are correlated with behavior based on test results from control and record sampling during the last two years. Correlation of the test results and the known behavior of aggregates in use for many years looks very promising.

• STONES, large and small, have been used for construction purposes for many thousands of years. In more modern times, engineers refer to the smaller sizes under the general term of mineral aggregates. Presumably, this sounds more scientific as it indicates that crushed stone, gravel or sand particles all consist of one or more minerals. Other phrases such as "the enduring stone" convey the idea that solid rock is unchanged by the vicissitudes of time, but both engineers and geologists know that rocky materials vary greatly in their ability to withstand the elements or to resist abrasive forces.

The money spent for mineral aggregates represents a large portion of the total money spent for construction, whether for buildings, dams or highway pavements and structures. Records indicate that between one-fifth and one-third of the funds expended for construction of highways in California is for the procurement and placement of aggregates; hence, with a budget of approximately $300 million for major construction during the fiscal year, this would result in $60 to $100 million for aggregates on State highway projects alone.

Production, processing, testing and control of aggregates are ever-present considerations in providing better highways for the traveling public. The complexity of the problems connected with aggregate production is increased by the depletion of the best and most convenient sources, by the necessity for considering beneficiation processes in aggregate production, and by the ever-present desire to secure good quality aggregates and at the same time keep the cost within reasonable limits.

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On the whole the producer prefers an aggregate that is easily and economically produced; the engineer likes for it to have ideal properties and structural characteristics; and the one who pays the bill wants it to be cheap and last forever.

The usual tests to control the quality of aggregates in California are grading, specific gravity, unit weight, absorption, soundness, Los Angeles rattler, R-value, cleanness, and sand equivalent. Generally, not all of these tests are applied to any one aggregate product. These tests are used on the premise that they will control the quality, suitability, and usefulness of the aggregate as well as these same attributes of the finished product that is produced from the aggregates.

Both the producer and the user are concerned with a characteristic of the aggregate that may be best described as "durability." Durability means, in the broad sense, the ability of the aggregate to remain unchanged over a fairly long period of time in spite of adverse natural processes or forces to which it is subjected. Specifically, the term durability as used here means resistance to breaking down or grinding up into finer particles.

As an indication of the concern over durability of aggregates, Washington, Oregon and Idaho have in recent years started using specific tests to measure this property. Many other public and private agencies are concerned with this problem and have considered or taken steps to assure more durable aggregates.

Considerable work has been done throughout the world in an attempt to develop a test method to evaluate resistance of aggregates to mechanical degradation. One of the earliest devices was the Deval Abrasion Test developed in France and, incidentally, a Deval tumbler was the first piece of testing equipment set up in the laboratory of the California Division of Highways in 1912. Probably the most widely used today is the Los Angeles rattler, developed about 1925. There have been various types of impact tests such as use of laboratory rollers, and piston-type crushing tests. However, whereas these various test methods will break down or tend to pulverize rock particles under test, the fine material produced generally differs markedly in character from the fines resulting from normal degradation on a roadbed. A fairly successful method of reproducing characteristic types of fines and aggregate breakdown in the laboratory has been accomplished through the use of a kneading compactor on samples containing considerable amounts of water. However, this type of laboratory determination requires considerable time and rather expensive equipment.

There have been a few clear-cut examples of failure or serious distress in California highways that could be attributed to deterioration or lack of durability of the aggregates. There have been other cases where breakdown of the aggregates was suspected as the cause of trouble but convincing proof is difficult to secure. Unless the entire operation is subjected to close control and frequent tests, a question always arises when excess fines are found; that is, were the fines introduced at the time of construction or did the aggregate lack the ability to withstand abrasive action and the subsequent weathering?

Probably most highway engineers can cite an example of aggregates that met specifications when placed in a stockpile but when these aggregates were incorporated in construction weeks or months later they would not meet the specifications. Again suspicions always arise as to whether the aggregates really met the specifications initially and subsequently degraded, that is, if the aggregate lacked the necessary durability to withstand the weathering and handling involved.

Figures 1, 2, 3 and 4 illustrate degradation or breakdown that can take place in the production and handling of aggregate. Figure 1 shows 1½- by ¾-in. stone as it left the plant where it met the cleanness specifications for concrete aggregate. The next three figures show changes in cleanness after successive steps in handling the aggregate. It would not meet the cleanness specifications in the condition shown in Figure 4. These pictures, which record one of California's first major encounters with the problem of aggregate degradation, were taken shortly after the cleanness value was introduced as a specification requirement.

The question of durability of aggregates has been emphasized in recent years in highway construction by the progress that has been made toward completion of the Interstate System. As a result of inquiries or investigations by various committees and agencies into highway construction practices, the question of durability or breakdown of aggre-

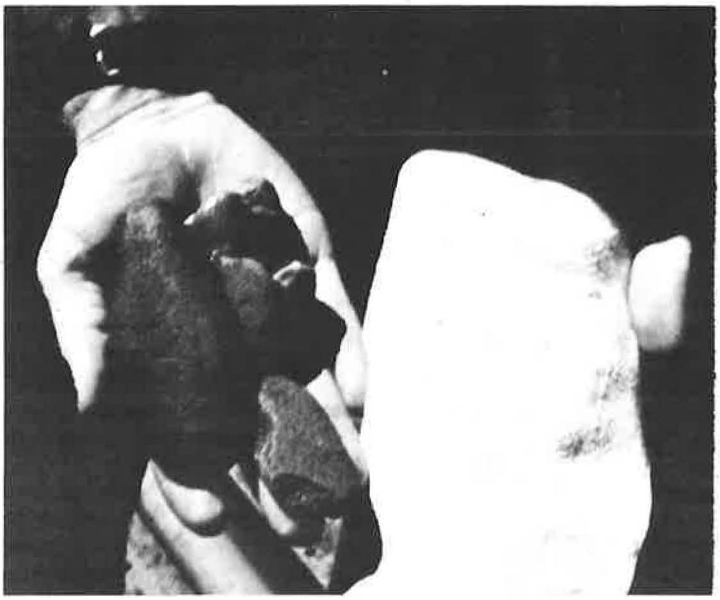

Figure 1. Degradation of $1\frac{1}{2}$- by $\frac{3}{4}$-in. pcc aggregate.

Figure 2. Degradation of $1\frac{1}{2}$- by $\frac{3}{4}$-in. pcc aggregate.

gates has been increasingly emphasized. The activities of these committees and other similar studies have generally evolved around the question of aggregates complying with specifications. There have been numerous investigations concerning the quality or thicknesses of aggregate layers in place. If an investigation indicates a certain grading or other test characteristic for an aggregate in place and previous tests indi-

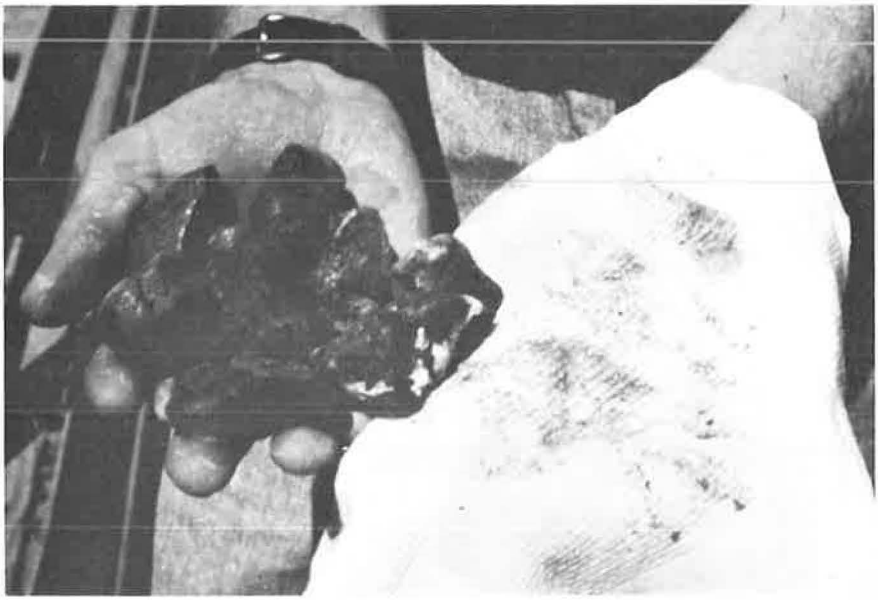

Figure 3. Degradation of $1\frac{1}{2}$- by $\frac{3}{4}$-in. pcc aggregate.

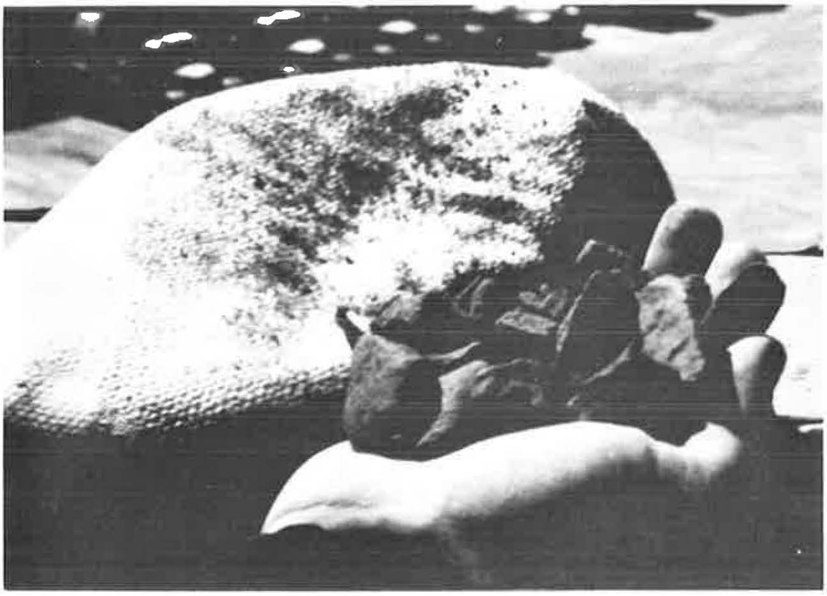

Figure 4. Degradation of $1\frac{1}{2}$- by $\frac{3}{4}$-in. pcc aggregate.

cate different characteristics before placing, a logical question is "What changes would normally take place as an aggregate is incorporated into a completed roadway?" To answer this question and at the same time move toward a more thorough knowledge of the characteristics of suitable aggregates, a durability test was developed by the California Division of Highways that will be incorporated in their new standard specifications.

TABLE 1

AVERAGE TEST RESULTS OF CONTROL AND RECORD SAMPLES ON AGGREGATE BASES

Contract No.	No. Locations	Control or Record	Avg. Passing Sieve (%)					Avg. Sand Equiv.	Avg. R-Value	Durability Index	
			1½ in.	¾ in.	No. 4	No. 30	No. 200			Coarse D_c	Fine D_f
61-3T13C15-F	2	C	94	68	34	20	4	50	80	87	86
		R	93	72	38	22	4	50	82		
61-7X13C15-P	3	C	100	98	50	22	7	66	79	80	80
		R	100	99	56	26	9	59	82		
61-6X13C54-F	2	C	100	94	44	23	6	47	76	87	78
		R	100	96	51	28	8	54	82		
61-3T13C31	6	C	97	80	37	15	4	47	80	78	74
		R	98	81	38	16	4	39	82		
61-6X13C52-P	5	C	99	67	40	24	6	66	80	85	70
		R	100	69	42	25	7	58	79		
61-11V13C7-F	3	C	96	75	47	22	10	31	80	66	68
		R	97	73	46	21	9	33	79		
61-10X13C32-P	5	C	91	77	52	24	8	48	79	67	66
		R	93	78	53	25	6	49	80		
62-2T13C2	2	C	96	77	52	22	8	44	81	63	69
		R	98	84	57	25	10	40	82		
62-10T13C1	3	C	100	95	49	25	7	31	79	59	65
		R	100	94	48	26	7	31	79		
61-4X13C38-P	3	C	100	63	24	11	6	28	81	67	57
		R	100	81	37	17	9	32	80		
61-3TC3	5	C	97	67	38	20	7	40	79	62	57
		R	97	71	41	22	10	40	81		
62-6Y24C3	3	C	96	86	67	30	13	31	79	54	51
		R	97	91	74	31	14	33	80		
61-9X13C12-P	4	C	100	96	51	30	12	37	81	59	48
		R	100	96	55	30	11	44	79		
60-6TC13-FP	5	C	100	96	58	31	9	32	80	59	44
		R	100	96	56	31	8	30	80		
61-1TC6	4	C	96	73	38	15	6	35	81	52	40
		R	98	81	48	22	10	26	74		
60-1DDC15-P	4	C	88	60	25	15	7	24	78	40	43
		R	97	74	39	24	10	25	79		
61-4X13C35-P	1	C	99	81	39	20	5	38	78	35	28
		R	99	85	45	25	9	27	82		

Tables 1 and 2 show grading, sand equivalent, R-value and other data secured in California's durability study. One set of data was secured from construction control samples as the various components of the roadway section were constructed. The other set of data was secured from final record samples after the roadway had been completed. Perhaps a third evaluation that is needed and may be secured to a limited extent would be from tests after these roads have been in service for many years. The above data are not always conclusive because the frequency of sampling is too limited to get good statistical values. Generally the final record samples show a breakdown of the aggregate, that is, finer gradation and lower R-value and sand equivalent. The data also show that this breakdown can be related to results of this new durability test.

It may be noted that some inconsistencies exist in the attached tables, particularly in the average grading analyses between the control and record samples for aggregate subbases. This can probably be best explained by the fact that most subbase control samples were obtained from a windrow, and it could not be established with any degree of certainty where the material represented by the control sample would be placed and compacted on the roadbed. This coupled with the probability of segregation during placing and grading variations in each load of material, may account for those data showing a coarser grading in the record sample than was found in the control sample. Because most of the base control samples were obtained immediately after being deposited on the roadbed from a spreader box, a better determination of the actual location of the material represented by the control sample was obtained.

One of the early phases of this durability study was the compaction of aggregate samples and subsequent testing to determine the changes in test characteristics. Aggregates were compacted using efforts far in excess of that required for normal compaction in order to accelerate the normal breakdown and then the resulting materials were tested to compare the new characteristics with the former characteristics.

TABLE 2

AVERAGE TEST RESULTS OF CONTROL AND RECORD SAMPLES ON AGGREGATE SUBBASES

Contract No.	No. Locations	Control or Record	Avg. Passing Sieve (%)					Avg. Sand Equiv.	Avg. R-Value	Durability Index	
			1½ in.	¾ in.	No. 4	No. 30	No. 200			Coarse D_c	Fine D_f
60-3TC37-F	2	C	94	75	42	28	4	68	77	86	85
		R	92	72	39	23	4	60	82		
61-3T13C18	2	C	100	92	76	62	6	75	69	90	81
		R	100	94	76	65	8	68	74		
62-10Y24C01	3	C	–	–	100	88	12	39	70	–	79
		R	–	–	100	88	15	34	70		
61-1T13C16	2	C	82	62	35	14	3	42	80	73	67
		R	88	69	40	16	4	37	83		
61-3T13C35-F	1	C	63	54	44	28	8	29	80	74	66
		R	52	34	27	18	6	24	80		
62-2T13C2	1	C	85	69	44	20	7	45	81	63	69
		R	95	77	51	27	8	39	83		
60-3TC38	3	C	92	64	42	30	7	37	81	78	62
		R	90	55	35	25	8	29	77		
60-3TC24-FIPD	1	C	96	79	57	39	7	48	81	61	74
		R	96	73	52	34	7	54	76		
61-4X13C39-P	2	C	100	82	38	18	8	38	80	66	52
		R	100	86	48	21	10	36	82		
60-5VC11-F	3	C	–	–	–	100	12	29	70	–	49
		R	–	–	–	100	13	27	72		
62-10T13C1	2	C	99	92	68	36	6	38	75	48	63
		R	100	93	66	36	6	35	68		
62-11V13C4-F	1	C	100	98	85	34	11	54	77	–	45
		R	100	100	97	46	16	39	74		
61-6X13C51-F	4	C	–	100	96	49	12	46	71	–	40
		R	–	100	97	50	14	40	68		
60-5TC10	2	C	100	76	50	22	6	32	76	38	58
		R	100	80	52	24	8	30	79		
61-5X13C26-P	5	C	100	99	93	46	12	50	75	–	35
		R	100	100	94	48	14	39	75		
61-10T13C18	3	C	100	100	100	48	15	58	69	–	30
		R	100	99	98	51	16	44	68		
61-4MBC1	1	C	100	68	27	14	8	22	80	36	28
		R	100	90	52	27	14	23	71		
61-4X13C38-P	2	C	89	56	34	26	9	40	81	13	21
		R	97	80	56	44	16	28	76		
61-4T13C26-P	10	C	100	88	51	23	10	36	78	12	26
		R	100	92	58	29	12	33	77		
62-2Y24C05-P	2	C	90	77	45	30	16	32	59	8	18
		R	98	89	66	50	27	18	50		

In addition to routine sieve analyses and sand equivalent tests, the R-values of these materials were determined before and after laboratory compaction. The California resistance (R) value test measures the internal resistance to plastic deformation of a laboratory-fabricated saturated specimen subjected to a vertical load. The saturated test specimen is placed in a Hveem stabilometer and a load of 160 psi is applied vertically. The resultant lateral pressure transmitted through the specimen, read from the stabilometer gage, is used in determining the resistance or R-value of the material. The R-value may range from 100 for a nonyielding specimen such as steel to 0 for a material having no internal resistance.

Some of the results of this phase of test research are summarized in Table 3 and illustrated by Figures 5 through 15. Figure 5 shows a summary of the changes in R-value that results from excessive compaction of certain aggregates, whereas Figures 6 through 15 show test data comparing actual degradation occurring between control and record samplings with the same material degraded in the laboratory compactor. It should be noted that, although a somewhat higher degree of particle breakdown was achieved in compacting the material in the laboratory, particularly in the finer sizes, the general shape of the grading curves compares favorably with those of the field sample. An interesting relationship is indicated by examining the sand equivalent values of the control samples compared to those values on the same materials sampled from the road after compaction, that is, final record samples. Examination indicates that those materials having lower values in the durability test are most likely to show the greatest reduction in the sand equivalent values as a result of handling and processing.

TABLE 3

SUMMARY OF LABORATORY DEGRADATION TESTS USING KNEADING COMPACTOR[a]
(1, 000 applications at 290 psi)

Sample No.	Type of Material	Sample Ident.[b]	Passing Sieve (%)				SE	R-Value	Durability Index	
			¾ In.	No. 4	No. 30	No. 200			D_c	D_f
60-2668	Base	T	100	56	30	4	68	82	87	86
		D	100	52	33	9	37	75		
60-2666	Subbase	T	100	61	29	5	—	—	86	85
		D	100	61	29	5	73	79		
61-4238	Subbase	T	100	99	90	5	78	58	—	81
		D	100	99	88	9	66	73		
62-3177	Base	T	100	45	22	6	49	83	87	78
		D	100	48	27	8	37	83		
61-1400	Base	T	100	51	20	5	43	79	78	74
		D	100	55	25	9	30	77		
61-4332	Base	T	100	54	27	7	67	80	78	74
		D	100	58	33	10	59	81		
61-4116	Base	T	100	97	56	21	29	74	—	73
		D	100	97	60	21	26	71		
61-3819	Subbase	T	100	60	24	5	46	—	73	67
		D	100	63	31	9	28	84		
62-3228	Base	T	100	58	29	10	37	83	73	67
		D	100	66	40	20	23	68		
61-3567	Base	T	100	56	36	13	40	81	65	78
		D	100	62	46	19	27	84		
60-3358	Subbase	T	86	56	36	9	42	82	78	62
		D	86	57	39	13	26	80		
61-4335	Base	T	100	49	28	10	25	81	76	62
		D	100	50	31	13	23	79		
62-3284	Base	T	100	41	19	10	34	84	67	57
		D	100	48	29	17	22	80		
61-1245	Subbase	T	100	97	49	15	44	71	—	35
		D	100	98	59	22	26	64		
60-2799	Base	T	100	46	16	8	34	79	40	33
		D	100	56	24	14	22	79		
62-2933	Subbase	T	100	58	15	4	52	81	38	33
		D	100	68	29	14	32	80		
62-4171	Base	T	—	100	77	31	35	78	40	31
		D	—	100	84	53	15	67		
62-1003	Base	T	100	51	24	8	30	80	29	29
		D	100	71	49	28	15	22		
61-1044	Base	T	100	48	24	6	39	84	35	28
		D	100	92	70	35	17	27		
61-2861	Subbase	T	100	34	16	7	32	82	26	27
		D	100	51	30	15	28	66		
61-2431	Subbase	T	100	67	39	20	24	56	27	26
		D	100	79	55	32	19	26		
62-3064	Subbase	T	100	72	49	25	19	57	43	25
		D	100	76	50	27	16	47		
62-1691	Subbase	T	100	45	22	12	22	82	23	24
		D	100	78	54	36	13	11		
61-5058	Base	T	100	36	16	8	24	79	22	28
		D	100	17	32	16	17	53		
61-5445	Subbase	T	100	31	11	7	30	81	20	25
		D	100	61	35	21	17	25		
61-3963	Subbase	T	100	43	10	7	33	80	19	26
		D	100	86	54	34	16	46		
61-843	Subbase	T	100	51	22	8	25	48	16	18
		D	100	80	54	38	13	8		
61-624	Base	T	80	37	21	7	37	81	62	57
		D	86	44	26	11	28	81		
61-3101	Base	T	100	60	28	13	29	83	57	62
		D	100	65	35	18	22	81		
62-4144	Subbase	T	100	70	42	18	34	81	52	50
		D	100	87	64	40	17	52		
61-1199	Subbase	T	—	—	100	12	28	65	—	49
		D	—	—	100	14	26	65		
61-4459	Subbase	T	100	97	39	11	47	—	—	45
		D	100	99	48	15	43	77		
61-1231	Base	T	100	46	21	6	34	79	59	44
		D	100	55	29	11	27	78		
62-1679	Base	T	100	42	21	10	—	—	48	43
		D	100	51	29	16	26	80		
61-3851	Base	T	100	51	18	4	42	80	48	41
		D	100	67	37	18	20	70		
60-2919	Base	T	88	48	19	7	37	82	52	40
		D	92	54	26	13	23	73		
61-1365	Subbase	T	—	100	50	14	43	71	—	40
		D	—	100	56	24	23	48		
61-3007	Base	T	100	38	24	11	27	81	40	43
		D	100	53	36	15	23	80		
60-3408	Subbase	T	100	66	28	8	35	73	38	58
		D	100	69	30	10	32	78		
61-506	Subbase	T	100	78	54	26	22	71	42	38
		D	100	79	56	32	16	42		
62-1685	Base	T	100	52	16	4	62	82	36	47
		D	100	58	25	10	31	83		
61-2788	Subbase	T	100	43	21	7	31	78	15	22
		D	100	87	60	31	20	30		
61-5444	Subbase	T	100	45	27	14	19	58	14	24
		D	100	74	61	37	11	30		
61-1483	Subbase	T	100	60	46	16	39	79	13	21
		D	100	93	80	33	19	43		
60-3950	Subbase	T	90	62	25	9	53	79	12	26
		D	95	69	41	21	21	54		
61-4154	Subbase	T	100	55	36	21	29	68	8	18
		D	100	83	69	50	14	43		
61-5123	Subbase	T	100	33	11	5	28	76	2	26
		D	100	72	44	24	8	56		

[a] With 1, 000 applications at 290 psi.

[b] T, values as used; D, values after laboratory compaction.

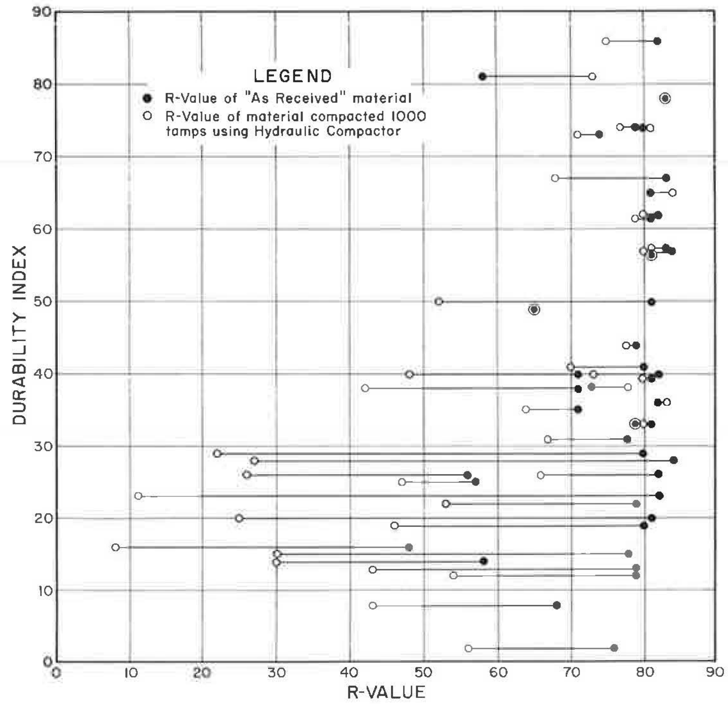

Figure 5. Reduction in R-value after laboratory degradation.

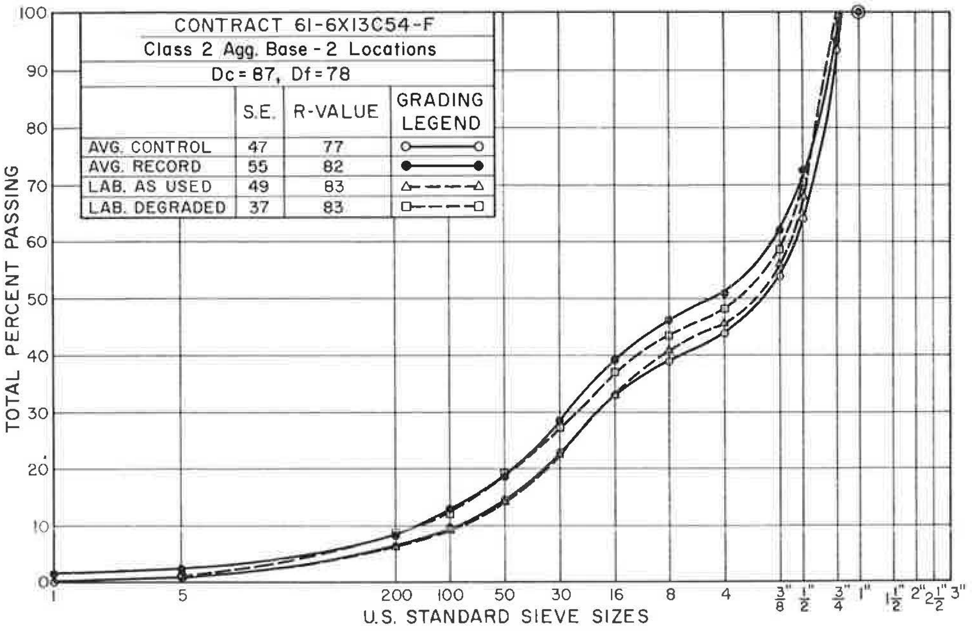

Figure 6. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

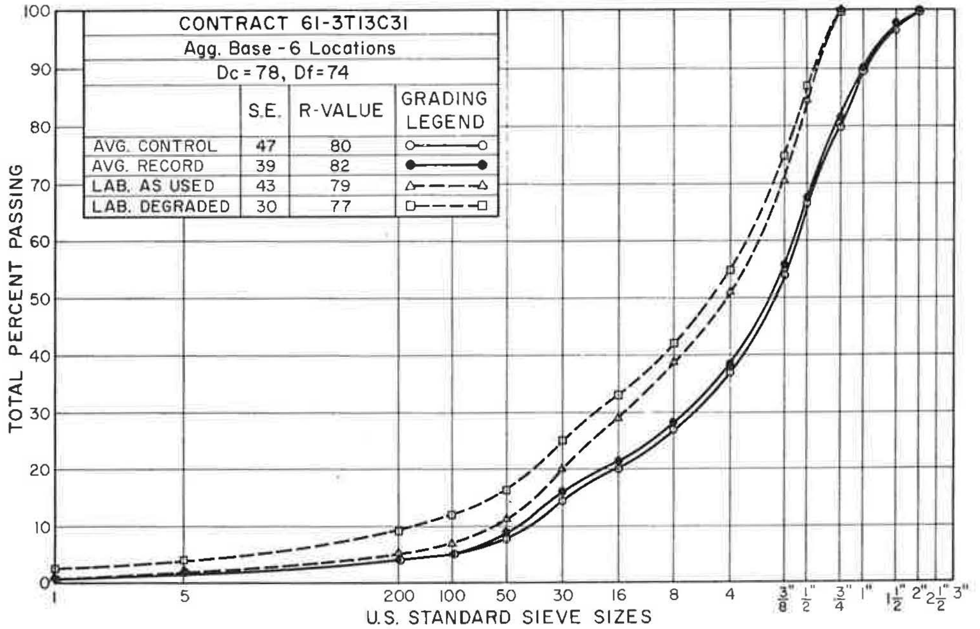

Figure 7. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

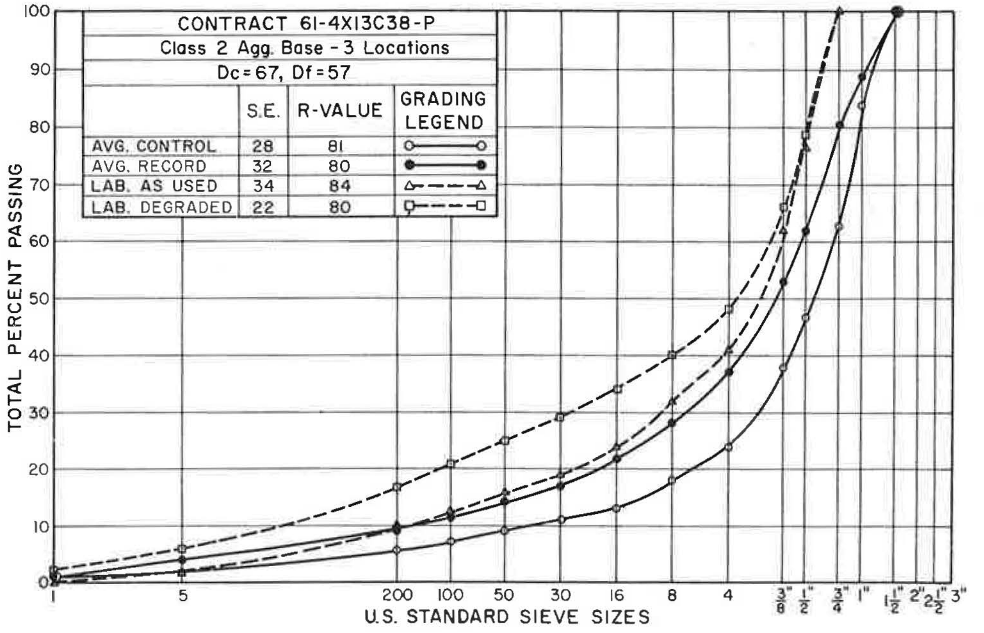

Figure 8. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

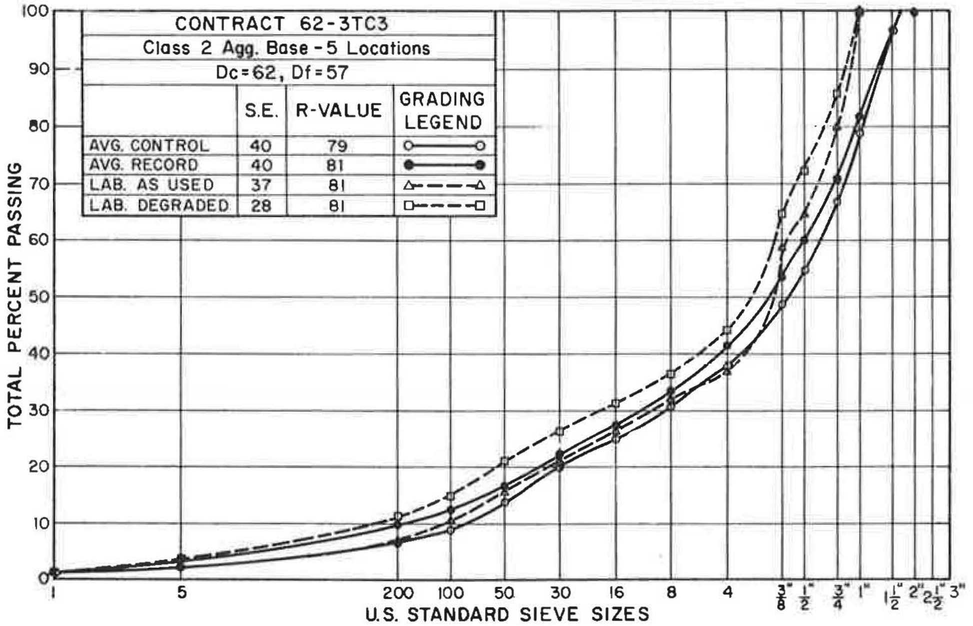

Figure 9. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

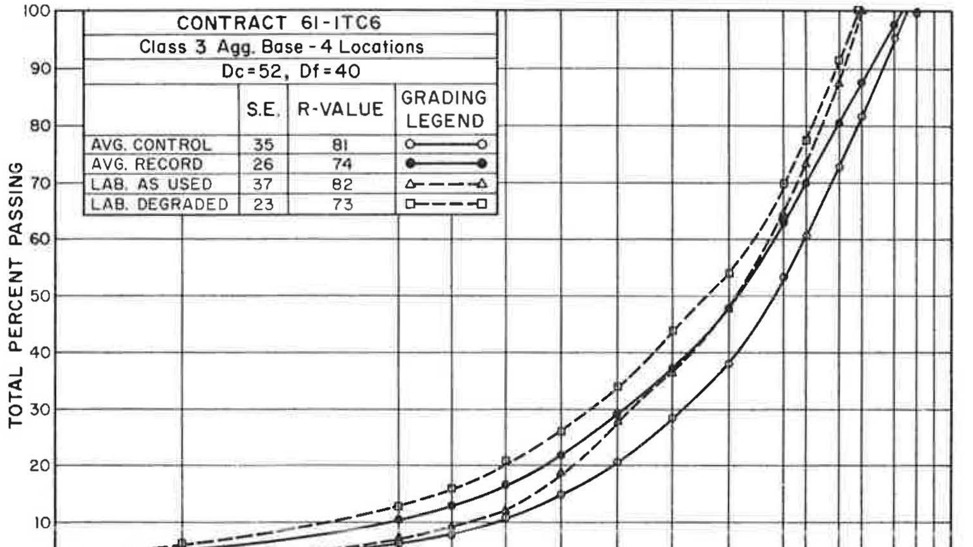

Figure 10. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

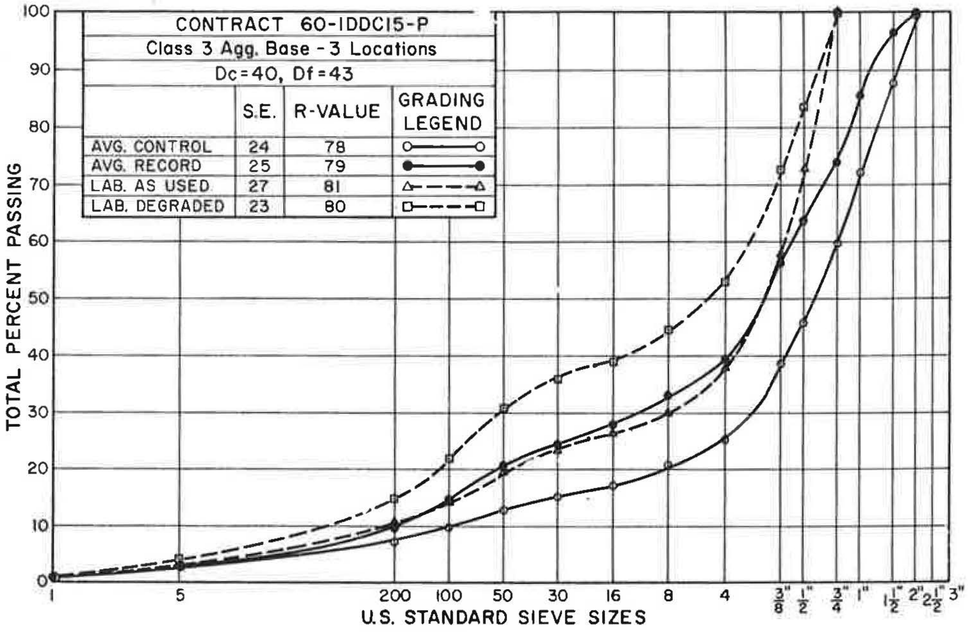

Figure 11. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

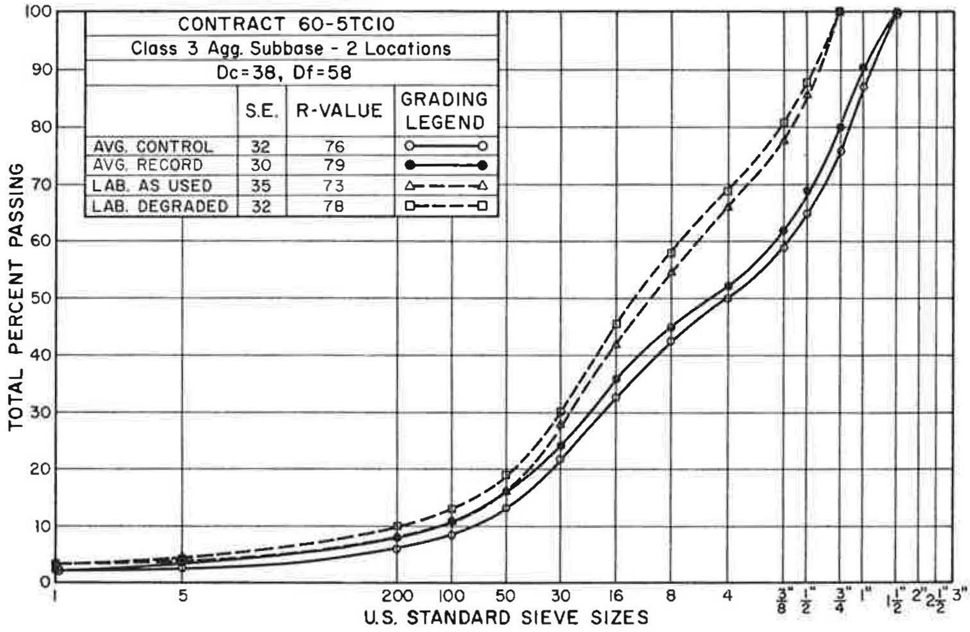

Figure 12. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

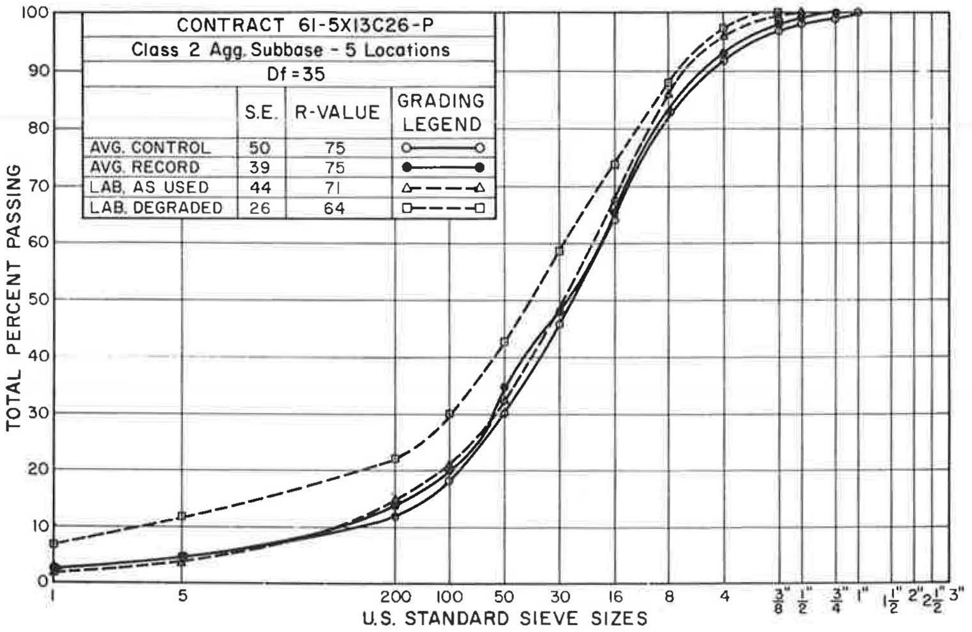

Figure 13. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

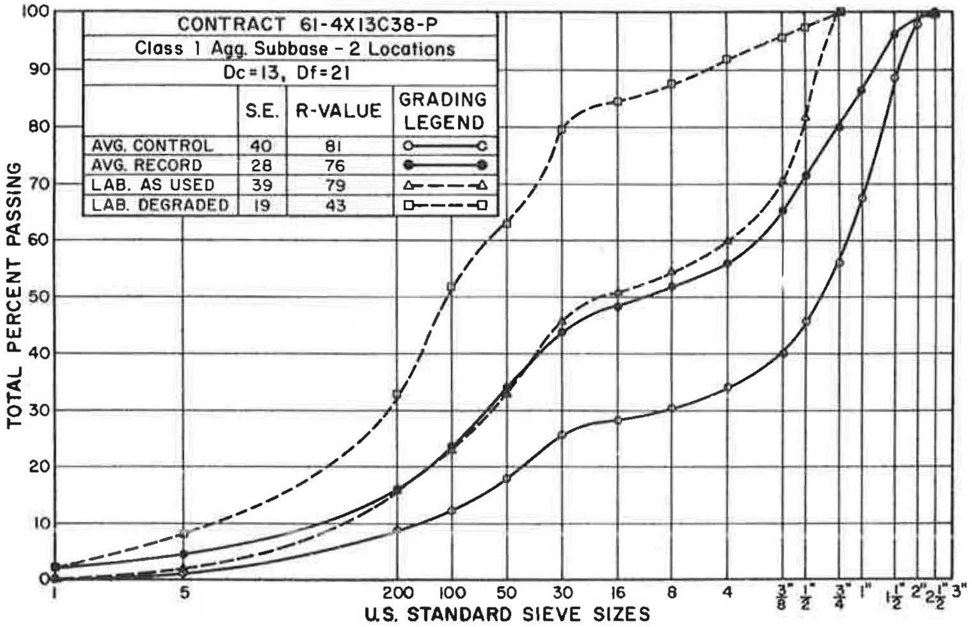

Figure 14. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

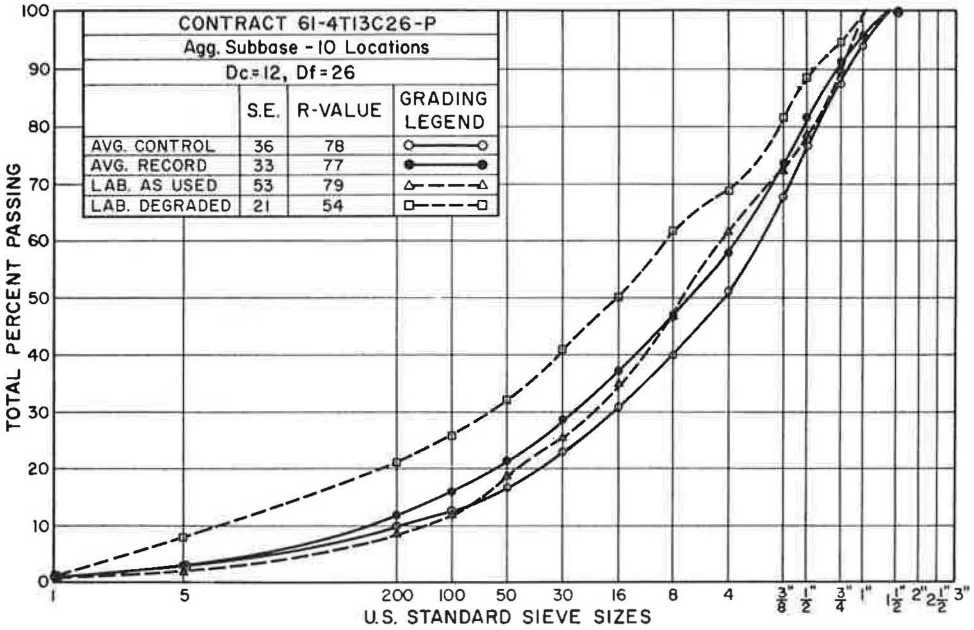

Figure 15. Comparison of changes in aggregate test values between construction placement and laboratory degradation.

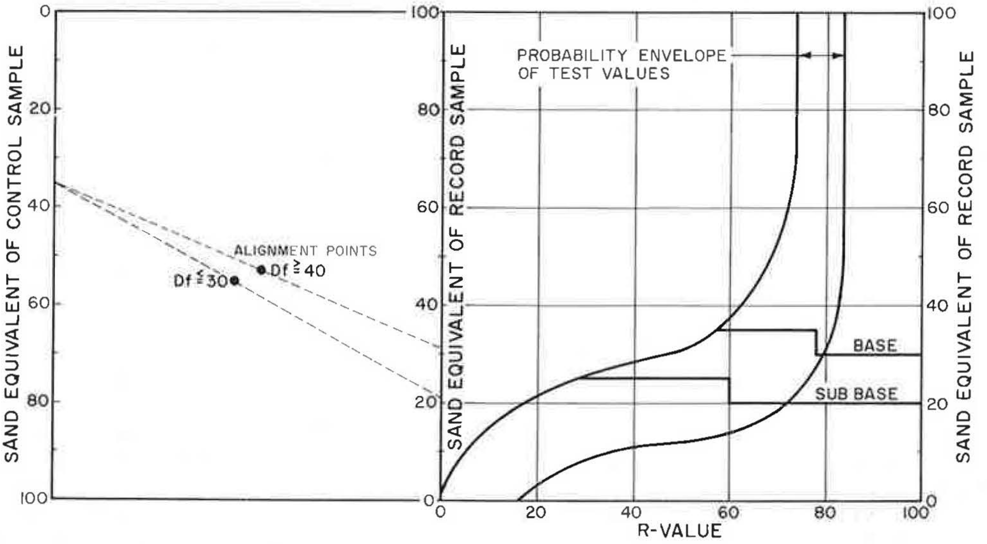

Figure 16. Interrelationships between sand equivalent, durability index, and R-value.

These relationships are indicated by Figure 16. It appears that if the durability index is known and the initial sand equivalent at the production plant is determined, it will then be possible to predict with considerable assurance the sand equivalent of the final record samples taken from the roadbed and, hence the probable R-value range which may be anticipated. This chart also illustrates the well-known fact that sand equivalent values in the neighborhood of 20 correlate very poorly with the R-value measurement. In other words, if sand equivalent values are 35 or better, high R-values are virtually assured. If the values are less than 15, it is practically certain that R-values will be low but with values between 15 and 35, R-values will have a wide range.

Whereas it is evident that the question of durability involves mechanical breakdown, natural weathering processes, chemical action, and probably other factors, this durability test reflects primarily the mechanical breakdown of aggregates evaluated in terms of a durability index. This index is a value indicating the relative resistance of an aggregate to producing detrimental clay-like fines when subjected to the prescribed mechanical methods of degradation.

The durability test method utilizes for the most part equipment developed for other routine tests developed by California; namely, sand equivalent and cleanness. Both of these tests indicate the amount, fineness and character of clay-like fines present in aggregates in the form of coatings or otherwise.

In the sand equivalent test, a small representative volume of the fine aggregate is placed in a graduated cylinder containing a calcium chloride solution. The cylinder is vigorously agitated for a specified time; then the material in the cylinder is "irrigated" to wash the clay-like fines into suspension above the aggregate. After irrigating the sample, the clay-like fines are allowed to settle for a prescribed length of time. At the end of this sedimentation period, the height of sediment, flocculated by the calcium chloride solution, is read and the height of sand is determined. The sand equivalent is determined by dividing the sand height by the sediment height and multiplying by 100. Sand equivalent values may range from 0 for a clay containing no material retained on a No. 200 sieve to 100 for a thoroughly washed sand containing no fines.

The cleanness test, for use on coarse aggregates, primarily those used in portland cement concrete, is performed as nearly as possible as the sand equivalent test is performed on fine aggregates. In the cleanness test, a representative portion of the coarse aggregate is washed by mechanical agitation for a specified period of time. Then a portion of the wash water containing the minus 200 sieve material in suspension is poured into a graduated cylinder containing a small amount of calcium chloride solution. The contents of the cylinder are thoroughly mixed and allowed to settle. At the end of the sedimentation period, the flocculated height of sediment is read and the cleanness value computed. As in the sand equivalent test, cleanness values may range from 0 indicating a large amount of highly active clay-like material present to 100 for an extremely clean aggregate.

Investigations made during and subsequent to the development of the cleanness test indicated that as the mechanical washing agitation period was increased, the resulting sediment height was also increased. Because this was true even though the aggregate was thoroughly washed before testing, it appeared that clay-like fines were being produced through degradation of the aggregate during the agitation period. These results paralleled earlier studies into the sand equivalent test procedure in which it was found that the inherent shaking techniques used by different operators resulted in wide variations in the sand equivalent value. Although this sand equivalent study resulted in California adopting a mechanical shaker for "referee" tests, it also disclosed that some action other than removing fines from the coarser particles was occurring during the agitation period.

Because the research test data obtained from studies of the cleanness and sand equivalent tests indicated that clay-like fines were possibly being produced during the agitation periods, over 300 samples of aggregate were obtained throughout California for this degradation study. Subjecting laboratory washed aggregate to extended periods of agitation produced clay-like fines similar to those present in compacted mixes which could be measured in the same manner as used in the cleanness and sand equivalent tests.

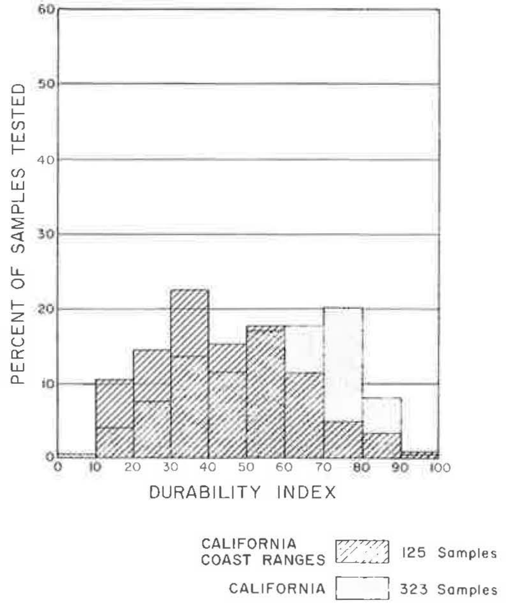

Figure 17. Frequency distribution of durability indices in California.

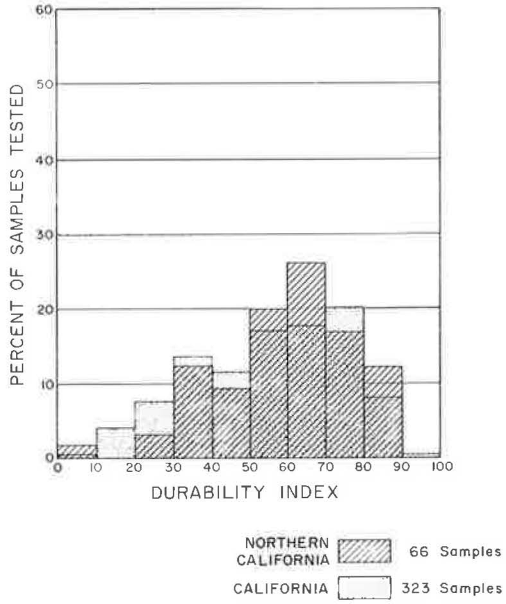

Figure 18. Frequency distribution of durability indices in California.

The result of California's aggregate degradation investigation was the introduction of this durability test procedure. Test samples are prepared from material that has been thoroughly washed in the laboratory. The durability test is then performed on these washed samples in the same manner as the cleanness and sand equivalent tests except the agitation times have been extended to 10 min and a new formula was derived for determining the durability index of coarse aggregate to make the coarse and fine values more compatible.

Durability indices for either coarse (D_c) or fine (D_f) aggregates may range from 90 for such hard materials as quartz down to 5 or less on clay-bound sandstones and shales. In California's standard specifications durability indices above 35 will be required for Class II and III bases and above 40 for Class I bases and permeable materials. In aggregates containing both coarse and fine fractions the durability index for both sizes must be above the required minimum. It should be emphasized that the durability test (by starting with a washed aggregate in the test sample) measures the quality of the product generated from interparticle abrasion during the agitation period. The fines in the original sample have no effect on the durability index. It is not presently anticipated that the durability test will be regularly specified for concrete aggregates or aggregates for asphalt surfacing.

Figures 17 to 20 show the results of numerous durability tests made on aggregate sources from the various regions throughout California. It will be noted that some areas have many sources that are low or marginal. Test values on many aggregates from the coast ranges, which are abundant in sandstone, serpentine and shale, are very low. On the other hand, the aggregates from Southern California show consistently high durability indices.

Figure 21 shows a grouping of test results by types of mineral aggregate and their corresponding durability indices. Some types of mineral aggregates generally show high test results where other types of mineral aggregates will show low test results. The higher test values were obtained on andesites, granites, and limestones, whereas the lower test values were obtained on sandstones and weathered volcanics. Many of the aggregates tested are of such a heterogeneous nature that it is difficult, if not impossible, to place them in the categories shown on this chart.

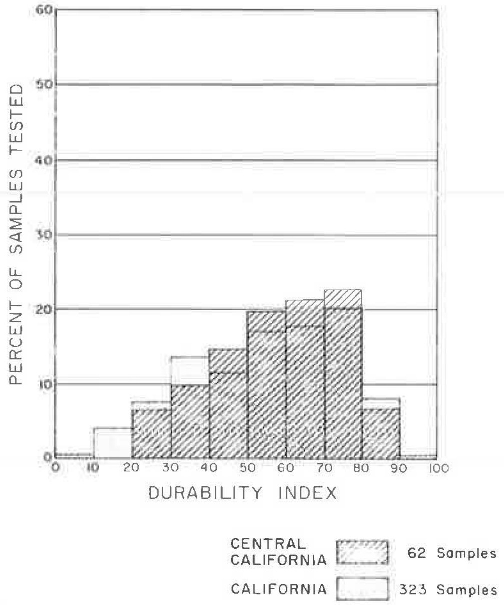

Figure 19. Frequency distribution of durability indices in California.

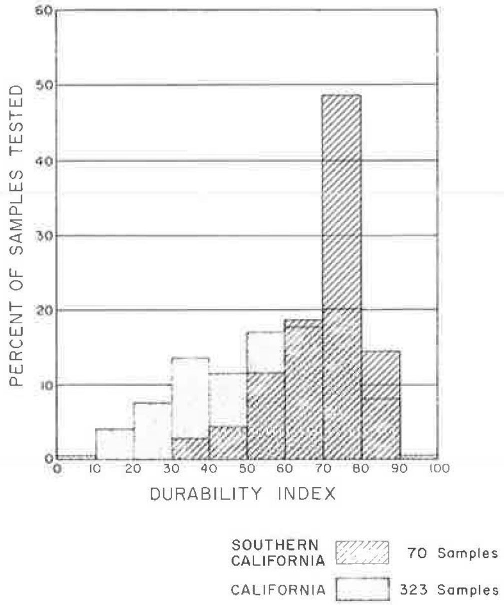

Figure 20. Frequency distribution of durability indices in California.

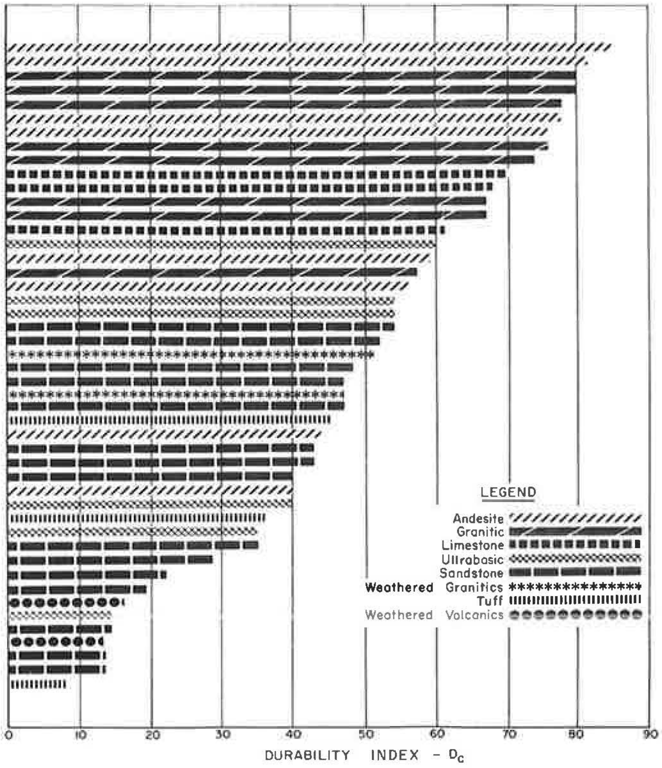

Figure 21. Durability indices of stone by petrographic classification.

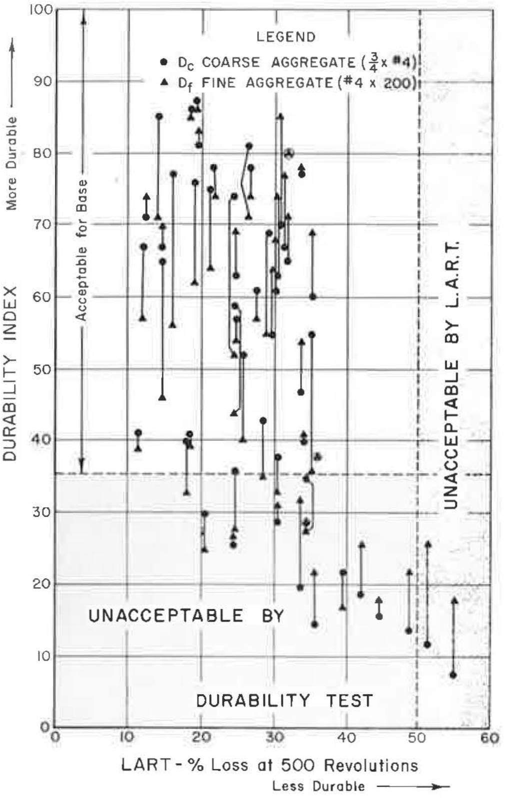

Figure 22. Comparison between durability indices and Los Angeles rattler loss.

Figure 22 shows the relationship between the Los Angeles rattler and the new durability test. The ordinate shows durability indices for both the coarse and fine aggregate portions, whereas the abscissa values show the Los Angeles rattler loss at 500 rev for the coarse materials. The very soft materials show up adversely in both tests, but there are certain samples meeting the present Los Angeles rattler requirements which break down when shaken in water for only 10 min. There is little or no correlation between the Los Angeles rattler and the durability index for the majority of materials shown in Figure 22. This is not surprising because the Los Angeles rattler test results are indicative of the quantity of degradation produced by an abrasion process involving considerable impact, whereas the durability test results reflect the nature of the degraded material produced as well as the quantity of degradation by an entirely different abrasion process.

The question will naturally arise as to what will be the effect of the introduction of this new durability test. Obviously, it will result in the rejection of some sources of aggregate presently used. This could be expected because some sources of aggregate have been troublemakers in the past and yet a test was not available that would eliminate these sources without the elimination of other known sources of good quality aggregate. The good correlation between known behavior of aggregate sources and test results has been most encouraging as the development of this test procedure has been completed.

The new durability test will be used in lieu of the Los Angeles rattler test on permeable materials and aggregate bases. Because some aggregates would not pass the present specifications for the Los Angeles rattler and these same aggregates will pass the new durability specifications, this will result in a relaxation of specifications in these instances. The relationship of R-value, grading, sand equivalent and durability in California's new specifications for bases will permit the use of some materials under these new specifications that were not acceptable under the present specifications.

The introduction of this new durability test should result in two steps toward effective use of aggregates with low or marginal durability characteristics. The quality of these materials can be improved by the use of additives and in many instances this will be the net result. Obviously, this step will usually be taken at the design stage; that is, designers will propose to use additives with aggregates with low durability indices. Figure 23 shows the results of successive durability tests made on several aggregates. There is a tendency for each durability test to give a higher test value than the preceding test. This is particularly true on aggregates with a low initial durability index. These results point to the beneficial effects of more vigorous washing and manipulating of the aggregates during production. Hence, if a given source has a low durability, durability of that particular aggregate source may be improved by more vigorous processing procedures.

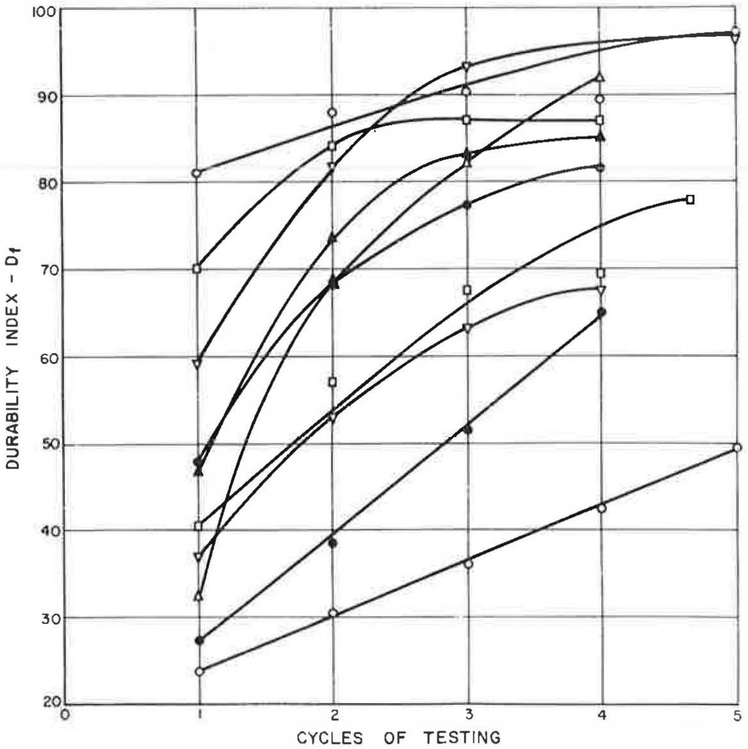

Figure 23. Effect of washing on durability index.

As discussed earlier, this new durability test procedure primarily reflects the breakdown resulting from mechanical manipulation. Continued efforts will be made to explore the effects of degradation due to other causes, such as weathering and chemical action, with the expectation of ultimately establishing test procedures that will realistically take into account all processes affecting the performance of the material on the road.

ACKNOWLEDGMENTS

Credit should be given to C. A. Frazier, Materials and Research Engineering Associate with the California Division of Highways, for his work in the development of the durability test procedure and the preparation of the data included in this paper. The major portion of the work was under the direction of A. W. Root, Supervising Materials and Research Engineer, who retired in May 1962.

Further Studies of Epoxy Bonding Compounds

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ABRIDGMENT*

• THIS REPORT is a study in detail of an epoxy formulation, Formulation G, which is suitable for application in the field of heavy construction. One type of such construction has been simulated by composite beam tests; however, the investigators feel that the most important part of the study has been the development of basic information concerning the physical properties of a single epoxy formulation, both as a plastic and as an adhesive, in several ranges of conditioning temperatures and curing times. An interim report, published in October 1962, gave information on Formulation G for specimen ages of 4 through 22 days in particular, and also gave some information for specimen ages of several months. This final report concentrates on filling in the basic information on the early ages of the specimens, and also presents information of long-term studies involving the aging and creep characteristics of the material.

Formulation G consists of the following:

Component	Parts by wt
Component A:	
Resin (equivalent epoxide weight 175-200, viscosity 10,000-15,000 cps)	100
Silica flour No. 219	12.5
Component B:	
Liquid polymer, LP-3	50
Silica flour No. 219	47.3
DMP-10	6.25
DMP-30	3.75
Bentone 38	2.5
Anti-foam 24 (General Electric product or equivalent)	2.5

Several important conclusions have been drawn from the results of this additional investigation. A few of these are as follows:

1. Changes in the conditioning history, especially during the early age of the formulation, significantly affect the results of physical testing.
2. At low temperatures the curing of the epoxy formulations is temporarily interrupted. At temperatures above 60 F, curing once again continues, and the material gains strength with time.
3. Prevention of the loss of water from the concrete is important during the early age of the concrete for optimum strength of the structural system.
4. To insure the full strength of the adhesive system, it is recommended that fresh batches of the components be prepared before field use. DMP-10 is predominately responsible for the deterioration of exposed stored components.
5. Formulation G, when used as an adhesive within the working stresses for composite construction, will creep negligibly, at least up to a loading time of 1,400 hr.
6. Changes in the normal thickness of an adhesive layer that would be used for field construction will not seriously affect the strength of the structural system.

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*Five copies of the complete paper have been sent to the Chief Administrative Officers of State Highway Departments. Additional copies are available from the Highway Research Board at $1.60 each.

Paper sponsored by General Materials Division.

7. The physical properties of Formulation G are not too much affected by changes in the particle size of silica flour 219.

8. Creep of a composite unit, consisting of a concrete slab glued to steel beams by Formulation G, was insignificant during a 6⅔ mo testing period.

9. The composite beams of steel-to-concrete using Formulation G as a shear connector showed excellent structural interaction under a slowly increasing live load to failure during a single loading condition. However, when severely loaded, unloaded, and reloaded to failure, they were weaker in strength than stud-connected beams tested under the same conditions of loading.