

ALTERNATIVES TO TYPE II CEMENT
Part I— Preliminary Laboratory Studies

by

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Research Engineer

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

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SUMMARY

In this study concrete mixtures incorporating fly ash are being investigated as possible alternatives to mixtures utilizing Type II cements. The mixture characteristics being considered are strength, resistance to freezing and thawing and sulfates, heat of hydration, and volume stability. Control mixtures are made of Types I, II, and III cements. In the experimental mixtures, Type IP cement — a blend of ordinary cement and fly ash — and Type I cement with fly ash as an admixture were used. This report gives the results of initial tests for compressive and flexural strengths, resistance to rapid freezing and thawing, early volume change, time of set, and heat of hydration. Long-term strength data and information on sulfate and scaling resistance and drying shrinkage will be presented in the final report, with recommendations from the study.

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INTRODUCTION

The Virginia Department of Highways & Transportation requires the use of Type II cement in all of its structures and pavements. Under certain restrictions, Type IP and Type III modified cements have been permitted.⁽¹⁾

The continued demand for Type II cement is attributed to its moderate sulfate resistance and low heat of hydration. Both of these characteristics are achieved without any additional cost as compared with ordinary Type I cements. In addition, Type II cements in Virginia have had a relatively low (less than 0.6%) alkali content, which has minimized or eliminated the possibility of deleterious chemical reactions between alkalies and aggregates. Unfortunately, it is anticipated that the demand for Type II cement will have to be met from a diminished supply brought about by environmental and energy conservation policies. While the restricted supply might be supplemented with cements of higher alkali contents being introduced onto the market as a result of recycling kiln dust during cement production, air pollution standards and increasing fuel costs will force older, inefficient plants to close and the rate of replacement with new facilities will be depressed because of soaring costs of construction.^(2,3) It is, therefore, essential that alternative materials be considered.

Substituting other cements for Type II or reducing the amount of it used in portland cement mixtures by incorporating additives or admixtures are possible solutions to the impending shortage. However, these alternatives should not be adopted at the expense of the qualities which make Type II cement so desirable.

Pozzolan is one material that can be used in portland cement mixtures to improve some of their properties.^(4, 5) It is a siliceous, or siliceous and aluminous material that in a finely divided state can combine with lime in the presence of water to form compounds possessing cementitious properties.⁽⁶⁾ The pozzolan can be artificial as in the form of fly ash, or natural, as in volcanic glass, pumicite, opaline shales and cherts, and calcined diatomaceous earth. Good pozzolan with a low carbon content used in optimum amounts can improve workability and sulfate resistance, produce low heats of hydration and thermal shrinkage, reduce permeability, and inhibit the deleterious reactions between certain aggregates and alkalies in cements.^(3, 5, 7, 8) Conversely, if a pozzolan is of poor quality or is used excessively, it can reduce the rate of hardening and strength development, increase water demand and drying shrinkage, and lower the resistance to freezing and thawing.

Among the available pozzolans is fly ash, a waste product found in abundant quantities in electric power plants that use pulverized coal as fuel. It consists of solid or hollow spherical particles of siliceous and aluminous glass, and, in smaller amounts, thin-walled, multi-faceted polyhedrons with a high content of iron particles and irregularly shaped porous carbon.⁽⁵⁾ When fly ash is blended or interground with cements at the plant, the end products

are marketed as Type IP cements. Such cements are covered by ASTM Specification C595-74. Fly ash can also be used as an admixture in the preparation of concrete mixtures. Even though it has not been utilized as an admixture in concrete by the Virginia Department of Highways & Transportation, a considerable experimental effort was directed toward its evaluation in the 1950's by the Research Council. (9-14) At that time it was found that problems regarding the uniformity of the material severely limited its use in concrete.

Ordinary cement blended or mixed with fly ash could provide the desirable properties provided by Type II cement and enable a flexibility in the choice of cementitious materials that would eliminate total dependency on one type of cement and reduce the amount of cement used in the mixture. As a result, considerable economic advantages in the building of highway structures could be gained.

OBJECTIVE AND SCOPE

The objective of this study is to evaluate some possible alternatives to Type II cement; namely, a Type I cement into which fly ash has been blended and a Type I cement to which fly ash has been added. The evaluation is based on the following characteristics of experimental concrete mixtures:

1. Compressive strength at 28 days,
2. resistance to freezing and thawing,
3. sulfate resistance,
4. heat of hydration, and
5. volume stability (freshly mixed and hardened concrete).

In that portion of the project reported here, the properties of potential alternatives utilizing blended IP cements and ordinary Type I cements incorporating fly ash were investigated by comparison with control mixtures utilizing cements of Types I, II, and III. A total of 416 cylinders, 96 prisms, 16 slabs, and 32 cylinder mortar specimens were fabricated from 48 batches of concrete.

The testing program included the determination of compressive and flexural strengths, sulfate resistance, freezing and thawing resistance, volume change, time of set, and heat of hydration. For the mixtures incorporating fly ash, a series of tests were performed to obtain the fly ash content yielding the highest strength for a fixed cement content. One hundred ten cylinders were fabricated and tested from 22 batches of concrete. The results of tests of compressive and flexural strengths up to 28 days, early volume change, time of set, resistance to rapid freezing and thawing, and heat of hydration are presented in this report. Long-term strength data along with information on sulfate and scaling resistance, and drying shrinkage will be included in the final report with recommendations resulting from the study.

PROCEDURE

Portland cement concrete mixtures containing Types I, II, III, and IP cements and Type I cement incorporating fly ash were proportioned using the absolute volume method. These concretes met the requirements of the Virginia Department of Highways & Transportation A3 (General Use) and A4 (Superstructure) concretes given in Table 1. Trial batching was performed to determine the mixture proportions for concretes with and without fly ash. In

concretes containing fly ash as an admixture, the amount of fly ash yielding the highest strength concrete was determined. (The fly ash was used as a replacement for a portion of cement.) The materials and the trial batching, including the optimum fly ash determination, are described below.

MATERIALS

In the fabrication of the A3 mixtures, each cement type used was obtained from two sources; for the A4 mixtures, only one source was used (see in Table 2). Cement D was Type I-II convertible meeting the ASTM Specifications for Type II cement, and is often referred to as Type II cement in this report. The chemical and physical analyses of the cements are given in Table A-1 of the Appendix. For air entrainment, a commercially available, neutralized vinsol resin solution was used. This solution was also used for the Type III A cement concretes to meet the entrained air requirement.

TABLE I

The Requirements for Virginia Department of Highways & Transportation
A3 (General Use) and A4 (Superstructure) Concretes

<u>Requirements</u>	<u>A3</u>	<u>A4</u>
Design Min. Lab. Com- pressive Strength at 28 days	3000 psi (20.7 MPa)	4000 psi (27.6 MPa)
Aggregate Size Number	57	57
Nominal Max. Aggregate Size	1 in. (25 mm)	1 in. (25 mm)
Min. Grade Aggregate	A	A
Min. Cement Content	588 lb/yd ³ (349 kg/m ³)	634 lb/yd ³ (376 kg/m ³)
Max. Water-Cement Ratio	0.49	0.47
Slump	1-5 in. (25-127 mm)	2-4 in. (51-102 mm)
Air Content	6±2%	6½±1½%

TABLE 2

Cement Types and Sources Used in A3 and A4 Mixtures

TYPE	SOURCE	A3	A4
I	A	X	X
I	B	X	
II	C	X	X
I-II	D	X	
III	E	X	X
III-A	F	X	
IP	G	X	X
IP	H	X	

The coarse aggregate was a locally available granite gneiss (Sp. Gr. = 2.78, Absorption = 0.5). Quartz sand (Sp. Gr. = 2.59, F. M. = 2.99, Absorption = 0.9) constituted the fine aggregate. In the mixtures containing fly ash as an admixture, Type I cement from source A and fly ash from two sources, one processed and the other unprocessed (designated P and U, respectively, and both meeting ASTM Specification C618-73) were utilized. The analyses of the fly ash are given in Table A-2 of the Appendix. The unprocessed fly ash was of good quality, as is evidenced by the fact it had a carbon content lower than that of the processed fly ash.

TRIAL BATCHING

Proportioning Mixtures Without Mineral Admixtures

Trial mixtures were made utilizing the minimum cement contents specified and adjusting the mixture water to yield a slump of $3\frac{1}{2} \pm \frac{1}{2}$ in. (90 ± 15 mm). This slump is recommended by the ASTM for the volume change tests and meets the requirements of the Virginia Department of Highways & Transportation. Based on the trial mixtures, A3 mixtures with Types I, II, III, and IP cements and A4 mixtures with Type IP cement were proportioned using the maximum allowable water and the minimum cement content shown in Table 1. In A4 mixtures with Types I, II, and III cements, 5% of allowable water was withheld to keep the slump within the specification. It was necessary to use a larger amount of air entraining agent in the IP mixture than in the control mixtures to attain the range of air contents specified.

Optimum Fly Ash for Strength

The addition of fly ash to the ordinary Type I cement mixtures was intended (1) to achieve economy by replacing a portion of the cement required for A3 and A4 concretes, and (2) to attain the desirable properties inherent in Type II cement mixtures. The partial replacement of cement by fly ash on equal volume or equal weight bases generally produces concretes with low early strengths (including that at 28 days) but high ultimate strengths. (4, 15, 16) However, a higher early strength can be obtained by adding fly ash in excess of the amount of cement eliminated and also by limiting the amount of cement removed. Initially, tests

were performed with fly ash to establish mixture proportions that yielded compressive strengths comparable to those of conventional A3 and A4 concretes at 28 days.

Small batches of concrete, $1/2 \text{ ft.}^3$ (14.2 dm^3), were proportioned utilizing 295.2 lb./yd.^3 (175.1 kg/m^3) of water, the maximum amount allowable in A4 concrete. To eliminate a variable, the initial mixtures were not air entrained. The amounts of cement and fly ash used to determine the optimum combination for strength are shown in Table 3. The mixtures were prepared utilizing both the processed and unprocessed fly ash.

TABLE 3

Amounts of Cement and Fly Ash Used to Determine the Optimum Fly Ash Content

Batch No.	Cement		% Cement Reduction Compared to		Fly Ash		% Fly Ash to Cement Plus Fly Ash
	lb./yd. ³	kg/m ³	A3*	A4**	lb./yd. ³	kg/m ³	
1	470	279.0	20	26	100	59.5	18
2	470	279.0	20	26	120	71.0	20
3	470	279.0	20	26	140	83.0	23
4	520	308.5	11	18	100	59.5	16
5	520	308.5	11	18	120	71.0	19
6	520	308.5	11	18	140	83.0	21
7	570	338.0	3	10	100	59.5	15
8	570	338.0	3	10	120	71.0	17
9	570	338.0	3	10	140	83.0	20

* A3 concrete cement content: 588 lb./yd.^3 (349 kg/m^3)

** A4 concrete cement content: 634 lb./yd.^3 (376 kg/m^3)

A limit was imposed on the amount of fly ash used because excessive fine material in the mixture could form a weak top surface layer and cause difficulties in maintaining the air and water requirements. To provide control specimens, A3 and A4 concrete mixtures without air entrainment were fabricated. All batches, with or without fly ash, were duplicated for assurance. From each batch five $3 \times 6 \text{ in.}$ ($75 \times 150 \text{ mm}$) cylinders were fabricated and cured in lime-saturated water until the age of test. Two specimens were tested for compressive strength at 7 days and the rest at 28 days.

The strength results presented in Figures 1 and 2 are for those processed and unprocessed fly ashes, respectively. The compressive strengths of the control specimens are shown by the horizontal broken lines. The results for the mixtures with fly ash substitutions indicate that strength values comparable to those for the control mixtures can be achieved in 28 days with considerable savings in cement. However, at 7 days the strength development in the mixtures with fly ash was less than that achieved in the control mixtures. Therefore, for the mixtures with fly ash, to attain strengths comparable to those of the A3 and A4 control mixtures, only very small reductions in the cement contents would be acceptable. From the results presented in Figures 1 and 2, it appears that different combinations of cement and fly ash can be used to obtain 28-day strengths comparable to those of the control mixes; however, for economy, the mixture utilizing the least amount of cement was preferred. The optimum amounts of cement and fly ash chosen are given in Table 4.

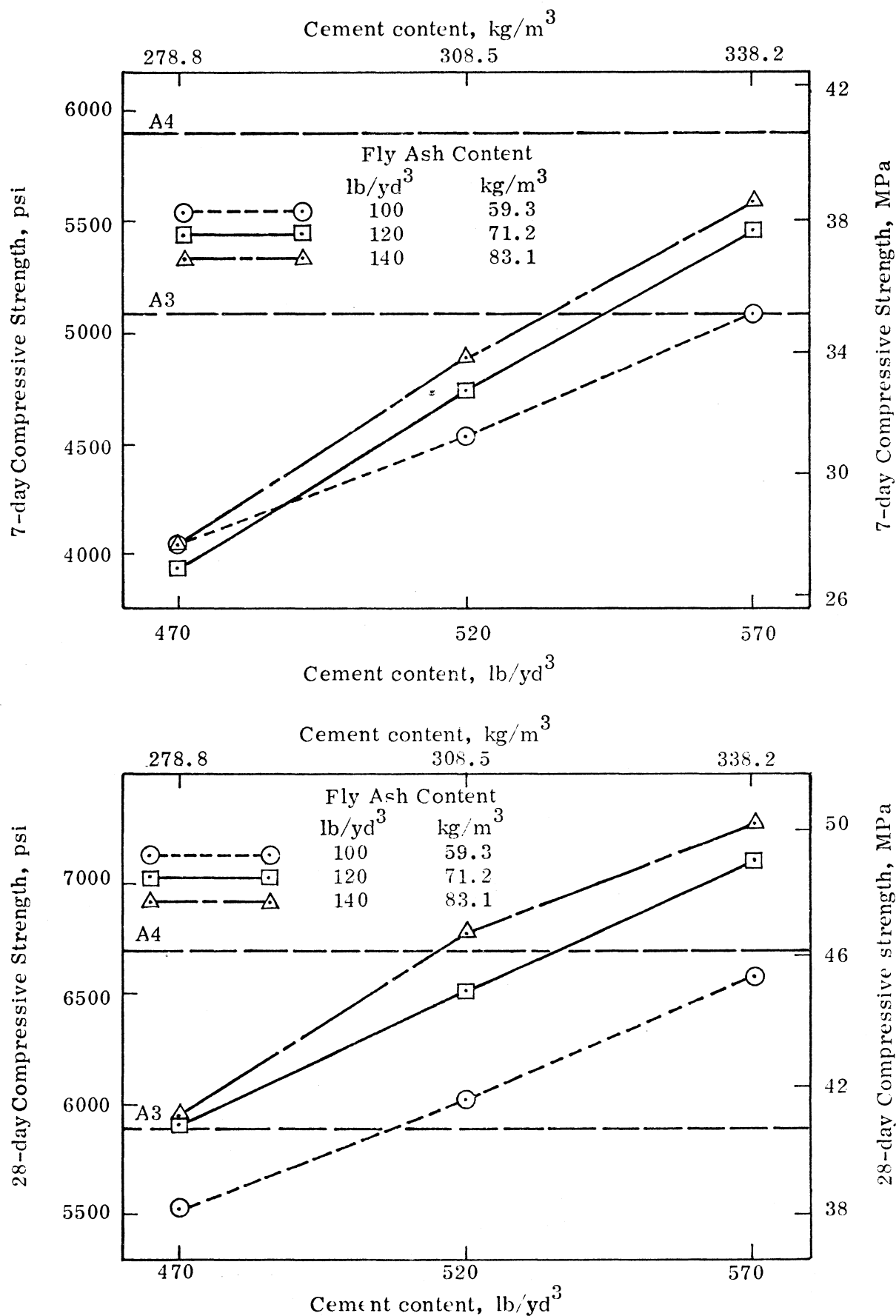


Figure 1. Compressive strength values of specimens utilizing processed fly ash at 7 and 28 days. Strength levels obtained by testing non-air entrained control A3 and A4 mixtures are represented by horizontal broken lines. Type I cement from source A.

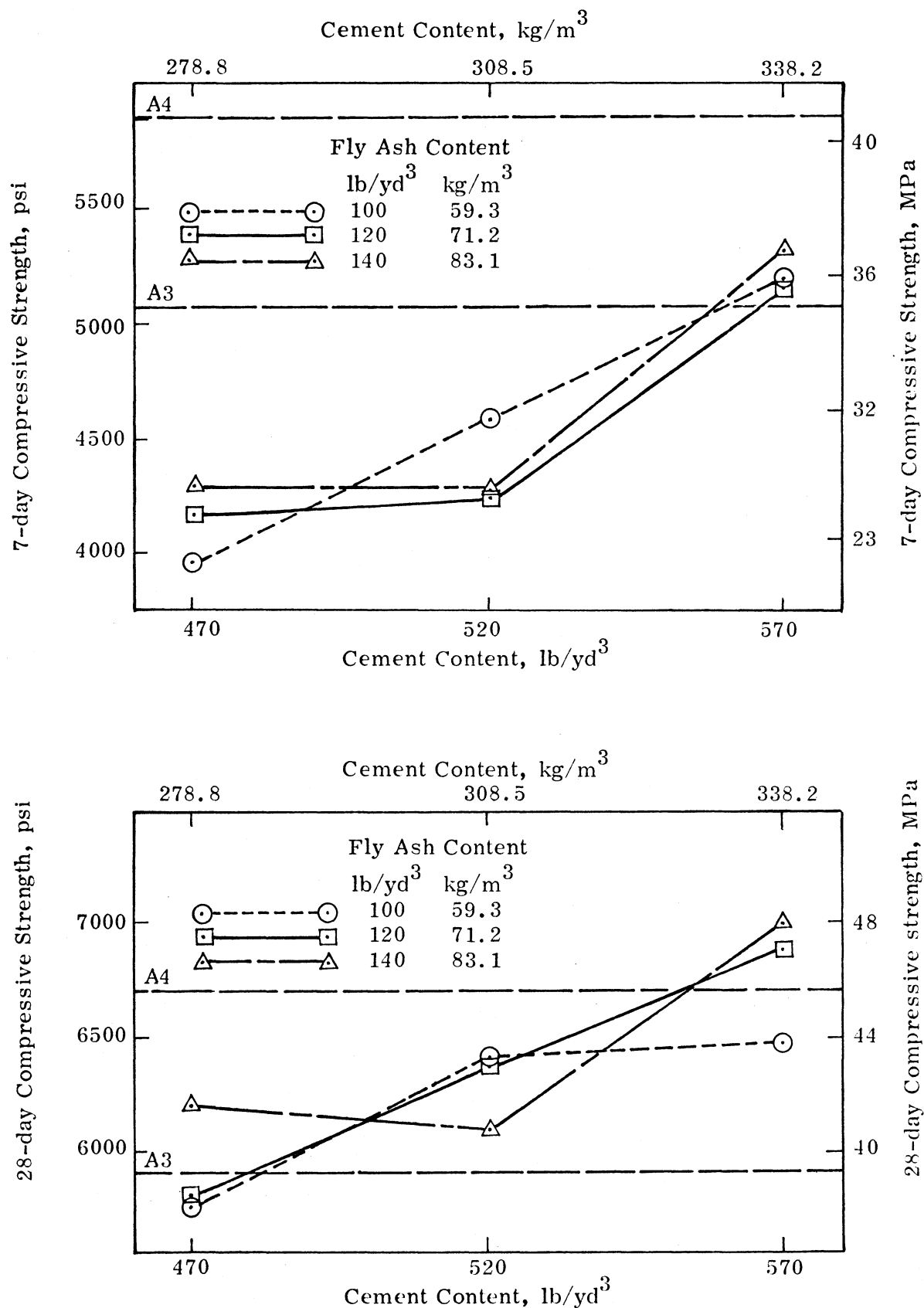


Figure 2. Compressive strength values of specimens utilizing unprocessed fly ash at 7 and 28 days. Strength levels obtained by testing non-air entrained control A3 and A4 mixtures are represented by horizontal broken lines. Type I cement from source A.

The mixtures utilized in the determination of optimum fly ash contents did not contain air entrainment, in the interest of eliminating a variable as mentioned before. Therefore, to fulfill the requirements of the Department, batches of concrete with air entrainment were prepared for only the optimum proportions presented in Table 4. Large amounts of air entraining agents, similar to the amounts used in the mixtures utilizing IP cements, were needed to achieve the air contents of A3 and A4 concretes. In the air entrained mixtures incorporating fly ash and representing class A3 concretes, 280 lb./yd.³ (166.1 kg/m³) of water were used; for those representing the class A4 concretes, 290 lb./yd.³ (172.0 kg/m³) were used.

TABLE 4

Optimum Fly Ash Contents

Class of Concrete	Type of Fly Ash	lb./yd. ³	<u>Cement</u> kg/m ³	% Reduction	<u>Fly Ash</u>	
					lb./yd. ³	kg/m ³
A3	Proc.	470	279.0	20	140	83.0
A4	Proc.	540	320.5	15	140	83.0
A3	Unproc.	470	279.0	20	140	83.0
A4	Unproc.	564	334.5	11	140	83.0

RESULTS OF GENERAL TESTING PROGRAM

After the establishment of the satisfactory mixture proportions for workability, air content and water-cement ratio, specimens were prepared from three batches in accordance with ASTM test method C192-69. The air content, slump, and unit weight of mixtures made with different cement types are given in Appendix Table A-3. The tests, related ASTM specifications sample dimensions, the method of evaluation, and the number of samples are indicated in Table 5.

The replicate batches were prepared on different days to eliminate or discover any possible time dependent errors. To determine the compressive and flexural strengths, sulfate resistance, rapid freezing and thawing, and drying shrinkage an average of three samples was obtained. The samples were randomly selected from the three batches as shown in Table 5. One sample was fabricated for each test to determine the resistance to scaling and freezing and thawing, early volume change, time of set and heat of hydration.

Compressive Strength

To evaluate the compressive strengths at different ages, 6 x 12 in. (150 x 300 mm) cylinders were fabricated and moist cured for testing at 7, 14 and 28 days and 6 months. The results from the 7, 14 and 28 day tests performed in accordance with ASTM C39-72 are given in Figure 3 and are summarized in Appendix Table A-4.

TABLE 5

Types of Tests and Number of Samples

Tests	ASTM Specification	Sample Dimension	Methods of Evaluation	No. of Samples			
				Batch 1	Batch 2	Batch 3	Total
Compressive Strength	C39-72	6 x 12 in. (150 x 300 mm)	Load to failure	2	5	5	12
Flexural Strength	C78-75	3 x 4 x 16 in. (75 x 100 x 400 mm)	Load to failure	1	3	5	9
Sulfate Resistance	*	3 x 6 in. (75 x 150 mm)	Weight & length change		2	1	3
Freezing and Thawing Resistance	C666-73	3 x 4 x 16 in. (75 x 100 x 400 mm)	Max. no. of cycles, change in dynamic modulus, weight loss	1	1	1	3
	C672-72T	12 x 12 x 3 in. (300 x 300 x 75 mm)	Surface rating		1		1
Early Volume Change	C827-75T	6 x 12 in. (150 x 300 mm)	Length change	1			1
Time of Set	C403-70	6 x 6 in. (150 x 150 mm) Mortar Specimen	Resistance to Penetration	1			1
Drying Shrinkage	C157-74	3 x 3 x 11 in. (75 x 175 x 280 mm)	Length change	2	1	3	6
Heat of Hydration	**	6 x 12 in. (150 x 300 mm)	Temperature change	1			1

* Refer to McGhee and Brown, and Polivka and E. H. Brown for the test procedure.

** Refer to Corps of Engineers CRD-C 38-73.

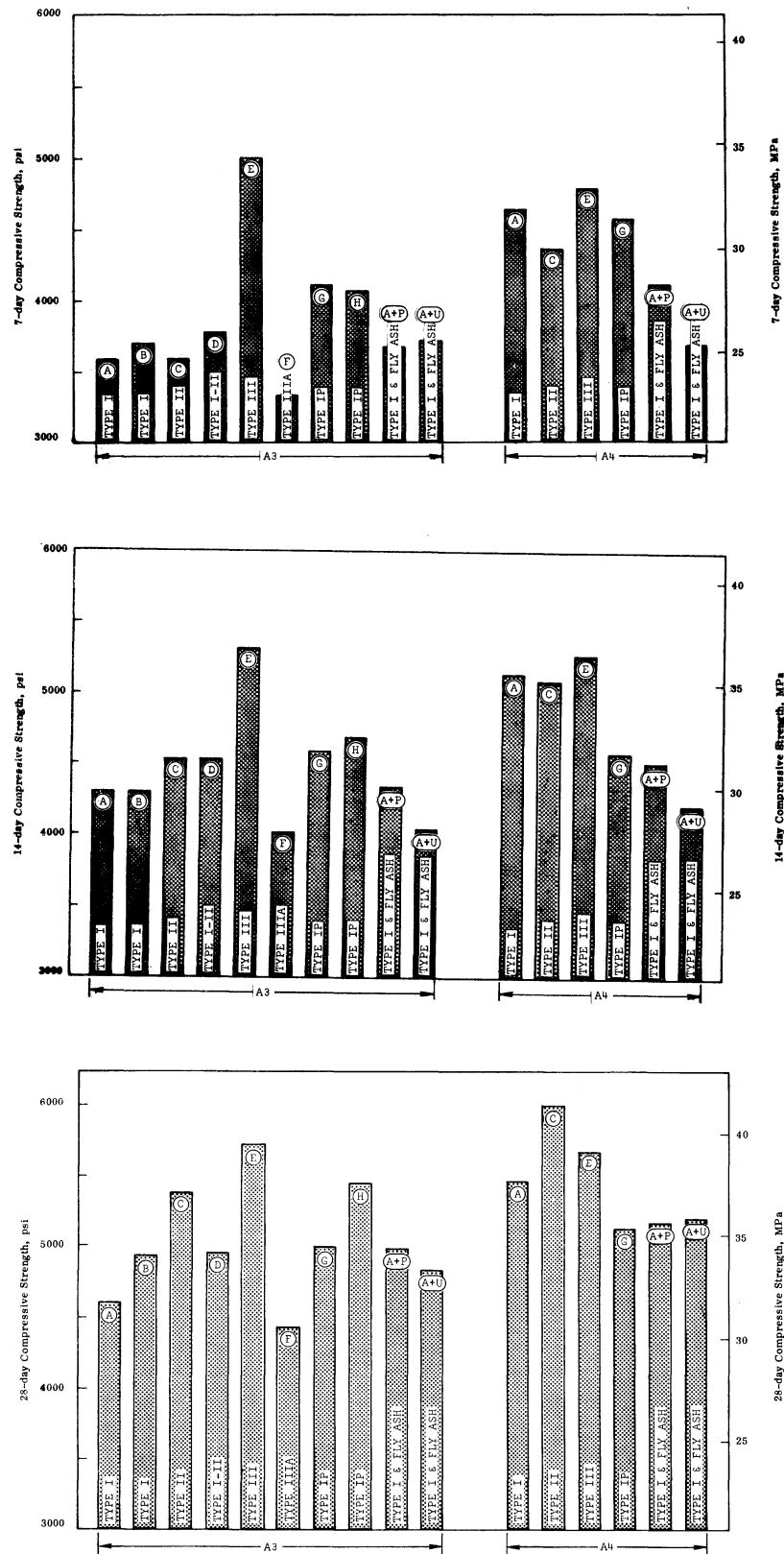


Figure 3. Compressive strength values

Figure 3. Compressive strength values.

Discussion of Compressive Strength Results for A3 Concrete

Mixtures with Type IIIA cement from source F attained the lowest compressive strengths, while the ones with Type III from source E gave the highest strengths. The lowest values were 3,340 psi (23.0 MPa) at 7 days; 4,020 psi (27.7 MPa) at 14 days; and 4,430 psi (30.5 MPa) at 28 days. The highest were 5,010 psi (34.5 MPa) at 7 days; 5,310 psi (36.6 MPa) at 14 days; and 5,730 psi (39.5 MPa) at 28 days.

Type IP and Type I mixtures incorporating processed and unprocessed fly ash and representing A3 concrete gave strengths comparable to those of Types I and II cement concretes at 7 and 28 days. Type IP cement mixtures yielded higher compressive strengths at 7 days, and this was attributed to the high cement fineness. Specimens made with Type III cement from source E attained relatively high strength at early ages as expected; however, the concrete made with IIIA cement from source F had the lowest compressive strengths found among the samples. In the lab test reports provided by the manufacturer, the Type IIIA cement had higher compressive strengths at 3 days than did the Types I, and I-II cements (sources B and D) of the same plant (see Appendix Table A-1). However, a lab test performed by the Department revealed a low compressive strength value of 2,655 psi (18.3 MPa) at 3 days for the Type IIIA cement sample. This value is lower than the minimum requirement of 2,800 psi (19.3 MPa) at 3 days specified in ASTM C150-74, and is in agreement with the low strengths achieved by Type IIIA cement mixtures.

Discussion of Compressive Strength Results for A4 Concrete

At 7 and 14 days, Type I mixtures incorporating the unprocessed fly ash gave the lowest strength values of 3,670 psi (25.3 MPa) and 4,220 psi (29.4 MPa), respectively; while the highest values of 4,770 psi (32.9 MPa) and 5,270 psi (36.3 MPa) were achieved by Type III concrete. At 28 days the highest strength of 6,000 psi (41.4 MPa) was achieved by Type II mixtures. Concretes made with Type IP and Type I cements and incorporating fly ash attained values lower than those of the control mixtures at 14 and 28 days. The 7-day results for the IP mixtures were comparable to those of the control mixtures and were higher than those for the mixtures incorporating fly ash.

Flexural Strength

ASTM Method C78-75 was followed to determine the flexural strength of concrete by the use of simple beams subjected to third-point loading. Concrete prisms 3 x 4 x 16 in. (75 x 100 x 400 mm) were prepared and moist cured for testing at 7 and 28 days and 6 months. The results of the 7- and 28-day tests are presented in Figure 4 and listed in Appendix Table A-4.

Discussion of Flexural Strength Results for A3 Concrete

At 7 days the flexural strengths varied from a low of 600 psi (4.1 MPa) for mixtures with Type IP cement from source G to a high of 745 psi (5.1 MPa) for Type I and Type III cements from sources A and E, respectively. At 28 days the lowest strength of 645 psi (4.4 MPa) was attained by IIIA mixtures. Mixtures incorporating fly ash achieved strengths comparable to those of the control Type II mixtures at 7 days. At 28 days samples made with Type II cement from source C reached slightly higher strengths than did the Type II cement from source D and Type I for both processed and unprocessed fly ash.

Discussion of Flexural Strength Results for A4 Concrete

At 7 days the Type IP mixtures and those with Type I incorporating fly ash gave lower values than did the control mixtures. Type I cement with the unprocessed fly ash gave the lowest value of 505 psi (3.5 MPa), based on the result from a single specimen. The highest strength of 780 psi (5.4 MPa) was achieved by Type III mixtures, followed closely by Type I and Type II concretes.

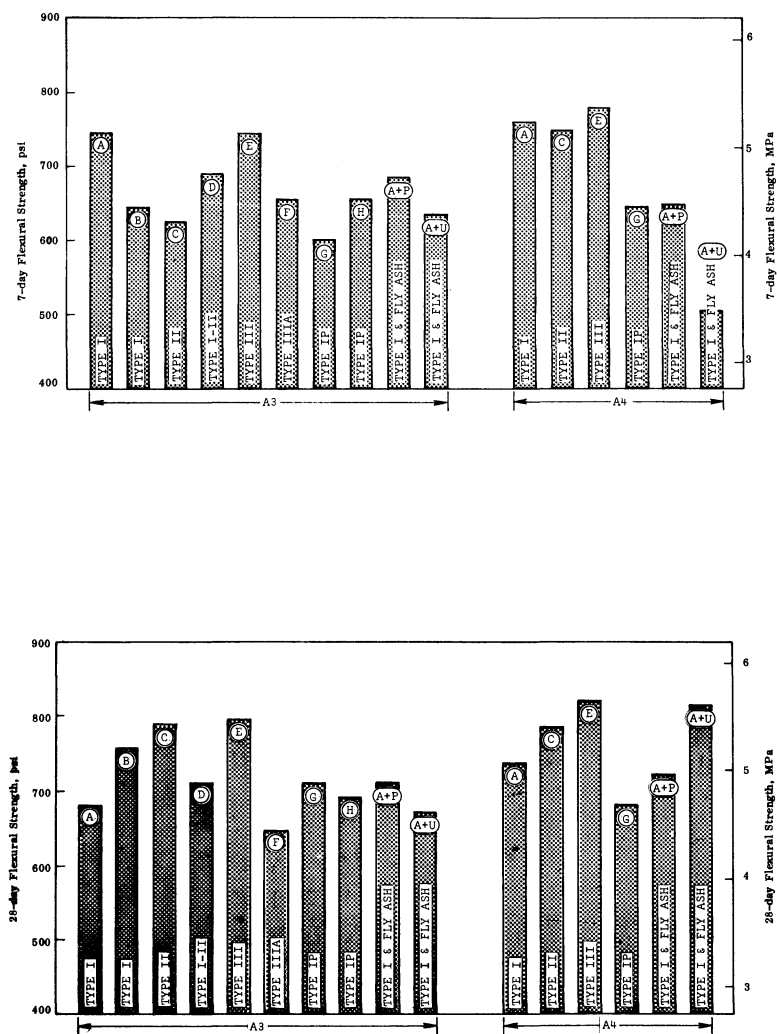


Figure 4. Flexural strength values.

Figure 4. Flexural strength values.

At 28 days the strength values varied from a low of 680 psi (4.7 MPa) for Type IP mixtures to 820 psi (5.6 MPa) for Type III cement, followed by 815 psi (5.6 MPa) for Type I incorporating unprocessed fly ash. In the mixtures incorporating fly ash, the ratios of flexural to compressive strength were similar to those of the control specimens as shown in Table A-4.

Freezing and Thawing Resistance

The resistance of concrete specimens to rapid freezing and thawing was determined in accordance with ASTM Method C666-73, Procedure A, except that 2% NaCl₂ was added to the water. Prisms measuring 3 x 4 x 16 in. (75 x 100 x 400 mm) were moist cured for 14 days and then air dried for 7 days. The relative dynamic modulus of elasticity, the weight loss, and the surface rating were calculated at the specified intervals. The test was continued until the specimens were subjected to about 300 cycles, or until their dynamic modulus of elasticity reached 60% of the initial modulus. The test was terminated in two cases when a weight loss exceeding 7% had occurred in order to save time and to prevent possible delays in the test program. The test results for the weight loss, the durability factor, and the surface rating based on an average of 3 prisms at 300 cycles are given in Table 6. The criteria suggested by prior research at the Council for satisfactory performance at 300 cycles are summarized in Table 7. (17)

Discussion of Freeze/Thaw Results for A3 Concrete

All the specimens prepared from the control Types I, II, and III cement mixtures and those incorporating fly ash met the criterion at 300 cycles except that the ones with Type I-II cement exhibited a surface rating of 3.1, which slightly exceeded the maximum acceptable value. Samples made with Type IP cements attained satisfactory durability factors indicative of good internal structure, but the surface ratings and the weight loss values were the highest among the A3 concretes. Weight losses of 7.0% and 7.4% occurred in the mixtures with IP cements from sources G and H, respectively. The surface ratings were 3.2 for the former and 3.1 for the latter mixture. In each of the Type IP cement concretes, one out of three samples showed excessive weight loss and the test was terminated for those particular specimens before 300 cycles were reached. These specimens were subjected to petrographic examination to determine the amount of air in the hardened concrete. It was found that the sample utilizing IP cement from source H had a low air content of 2.6% and a specific surface of 459 in.⁻¹, which indicates a low potential resistance to freezing and thawing. However, the sample with IP cement from source G had an air content of 5.7% and a specific surface of 857 in.⁻¹, which should provide adequate protection. Excluding these poor samples and averaging only two specimens, both IP cements yielded values within the aforementioned criteria.

Discussion of Freeze/Thaw Results for A4 Concrete

Satisfactory values for the weight loss, durability factor, and surface rating were obtained in all the A4 concretes. In general, concretes with low water-cement ratios, such as those representing the A4 concretes, had better resistance to surface scaling than did the corresponding A3 concretes. This trend was not observed in the concretes utilizing unprocessed fly ash. The two A4 concrete specimens incorporating unprocessed fly ash exhibited marginal performance. One of the two specimens was tested for air content and a low value of 3.9% was found. The third A4 concrete specimen with unprocessed fly ash underwent only a slight scaling.

TABLE 6
Rapid Freezing and Thawing Data
(Average of Three Specimens)

Cement Type	Source	Class	Wt. Loss %		Durability Factor		Surface Rating	
			300 cycles	Std. Dev.*	300 cycles	Std. Dev.*	300 cycles	Std. Dev.*
I	A	A3	0.9	0.3	99	1	1.7	0.4
I	B	A3	3.1	0.3	99	1	3.0	0.4
II	C	A3	2.0	0.8	99	1	2.5	0.3
I-II	D	A3	3.7	1.4	99	2	3.1	0.4
III	E	A3	4.2	2.0	98	3	2.7	0.7
IIIA	F	A3	2.7	0.8	97	3	2.6	0.5
IP *	G	A3	7.0	4.8	90	12	3.2	0.8
IP *	H	A3	7.4	4.2	98	3	3.1	0.6
I & Ash	A & P	A3	4.7	3.1	97	3	3.0	0.5
I & Ash	A & U	A3	3.7	1.0	95	3	2.4	0.1
I	A	A4	1.1	0.5	100	1	2.0	0.2
II	C	A4	1.7	0.4	98	4	2.1	0.4
III	E	A4	1.2	0.9	99	1	1.7	0.3
IP	G	A4	1.9	2.0	96	4	2.4	0.6
I & Ash	A & P	A4	1.8	0.6	98	4	1.8	0.4
I & Ash	A & U	A4	4.8	3.6	91	8	2.7	1.1

P = Processed Fly Ash
U = Unprocessed Fly Ash

* Testing of one specimen was terminated after it experienced weight loss in excess of 7% prior to 300 cycles. Then the weight loss, the relative dynamic modulus of elasticity, and the surface rating values were extrapolated to 300 cycles.

Mixtures containing fly ash, especially the Type IP cement concretes, exhibited lower resistance to deicer scaling than did the corresponding control mixes. They also showed more variable results as reflected by the standard deviation values given in Table 6. Perenchio and Klieger of the PCA state that concretes made with Type IP cements show less resistance to deicing scaling than do their counterpart Type I mixtures.⁽¹⁸⁾ However, they also conclude that the resistance to freezing and thawing in water is comparable for both Type I and IP mixtures.

The lower performance of the mixtures incorporating fly ash warrants further investigation. It is possible that the accumulation of fly ash at the surface causes a weak layer. To check this possibility, it might be desirable to conduct petrographic examinations on the surfaces of specimens prepared for drying shrinkage tests rather than using the freeze and thaw samples which already have lost the surface mortar.

TABLE 7

Criteria for Satisfactory Resistance to Freezing and Thawing

Cycles	Max. Wt. Loss, %	Min. RDF*	Max. Surface Rating**
300	7.0	60	3.0

* RDF = Durability factor

** Surface rating system used is:

- 0 = No scaling
- 1 = Very slight scaling 1/8 in. max. depth - no coarse aggregate visible
- 2 = Slight to moderate scaling
- 3 = Moderate scaling (coarse aggregate visible)
- 4 = Severe scaling

Early Volume Change

The volume change of concrete specimens restrained from lateral movement was determined during the plastic stage. The procedure utilized was an adaptation of the recently developed C827-75T, ASTM Tentative Method of Test for Early Volume Change of Cementitious Mixtures. Concrete was placed in cylinders measuring 6 x 12 in. (150 x 300 mm) in two layers. The outsides of the molds were tapped 10 times with a 3/8 in. (10 mm) diameter rod for consolidation. The cylinder was set on an optical bench and the test started within 13 minutes after the addition of mixing water. The optical setup was used to project an image onto a screen and magnify approximately 100 times the movement of an indicator ball located on top of the concrete. During the first 90 minutes, the movements were recorded at 5-minute intervals, for the next hour at 10-minute intervals, and thereafter at 20-minute intervals until the concrete hardened or a leveling off of the volume change occurred.

Figure 5 shows a typical graph obtained from the early volume change data wherein the early shrinkage in percentage is plotted against time. Generally, the curve increases sharply and then levels off. Since a very slight shrinkage was observed between 150 and 200 minutes, the test was terminated at 200 minutes. The maximum shrinkage values are shown in Figure 6 and the shrinkage data are tabulated in Appendix Table A-5 for time intervals of 50 minutes.

A3 concrete mixtures utilizing Type IP cement from source B gave the lowest shrinkage of 0.07% and Type I from source B yielded the highest value of 0.58% at 200 minutes. In A4 concretes the lowest shrinkage of 0.28% was observed in the sample made with Type III cement and the highest of 0.71% in the one containing Type II cement. A4 concrete mixtures made with Types I and II cements and Type I with fly ash and representing A4 concrete underwent a high early shrinkage compared to corresponding A3 mixtures, which indicates that a high cement content is accompanied by a high early volume change.⁽¹⁹⁾ However, for Type III and IP mixtures a reverse trend was observed. The variable results were sometimes contradictory; e.g., Type III mixtures yielded the lowest and Type II the highest shrinkage in A4 concrete, while Type IP and Type III mixtures gave lower shrinkage values in A4 mixtures rather than A3.

The shrinkage data are based on the testing of a single sample for each type of cement and more definitive results can be determined from further testing. Moreover, in the preparation of specimens the uniformity in consolidating the cylinders by just tapping the outside 10 times and the location of the indicator ball on the concrete surface where it may be close to or on an undetected coarse aggregate particle could easily affect the results. Utilizing more samples could alleviate or reduce errors; however, each test takes considerable time and requires an optical system.

In this study no attempt was made to correlate early volume change, heat of hydration, and the time of set because of the variability in the data and the use of only a single specimen in each case.

Time of Set

The time of set of concrete was determined in accordance with ASTM Method C403-70, Test for Time of Setting of Concrete Mixtures by Penetration Resistance. The time of initial set was recorded when a penetration resistance of 500 psi (3.5 MPa) was reached in a mortar sieved from concrete. Similarly, final set was taken as the elapsed time corresponding to a penetration resistance of 4,000 psi (27.6 MPa). The initial and final set values determined to the nearest five minutes from different mixtures are given in Appendix Table A-6 and in Figure 7.

Initial Set

In the A3 mixtures, a sample with Type IIIA cement attained initial set in the earliest time, 4 hours 45 minutes; and a sample with Type II cement from source C took the longest time of 6 hours 5 minutes. Type I mixtures incorporating fly ash reached initial set in about 5 hours. Among the A4 mixtures, a sample with Type I cement had the earliest initial set of 4 hours 15 minutes, while one with Type II cement had the latest at 5 hours 40 minutes. Mixtures with fly ash reached initial set in from 5 hours 5 minutes to 5 hours 30 minutes, and the IP mixtures required 5 hours 25 minutes.

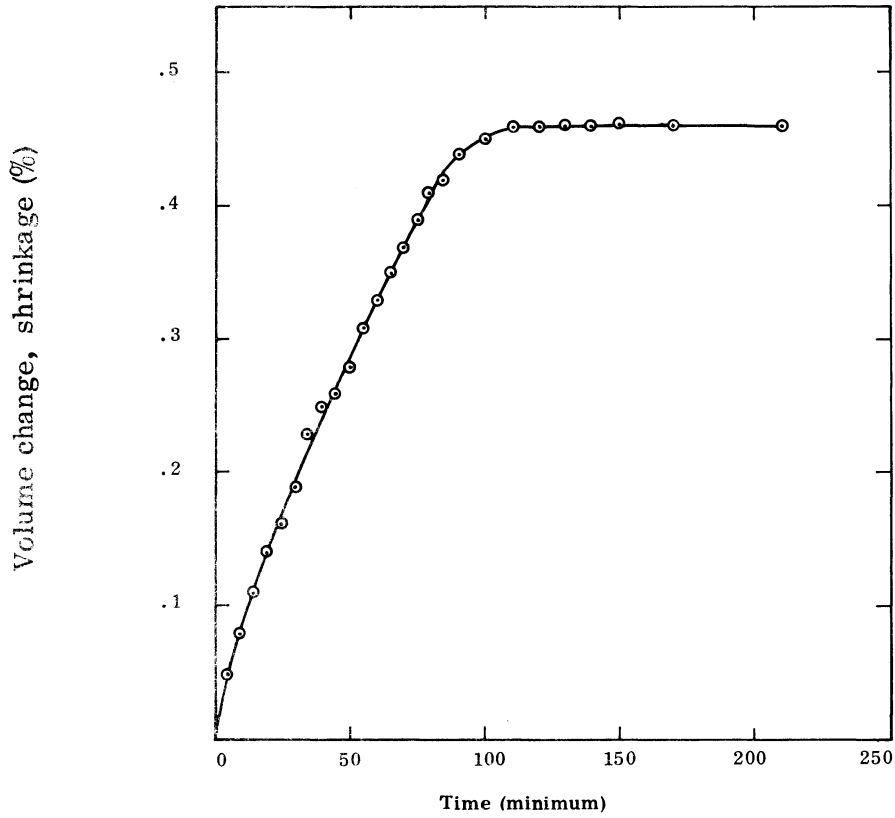


Figure 5. Typical early volume change curve for an A4 mixture prepared by Type I cement. Test starts 13 minutes after the addition of mixing water.

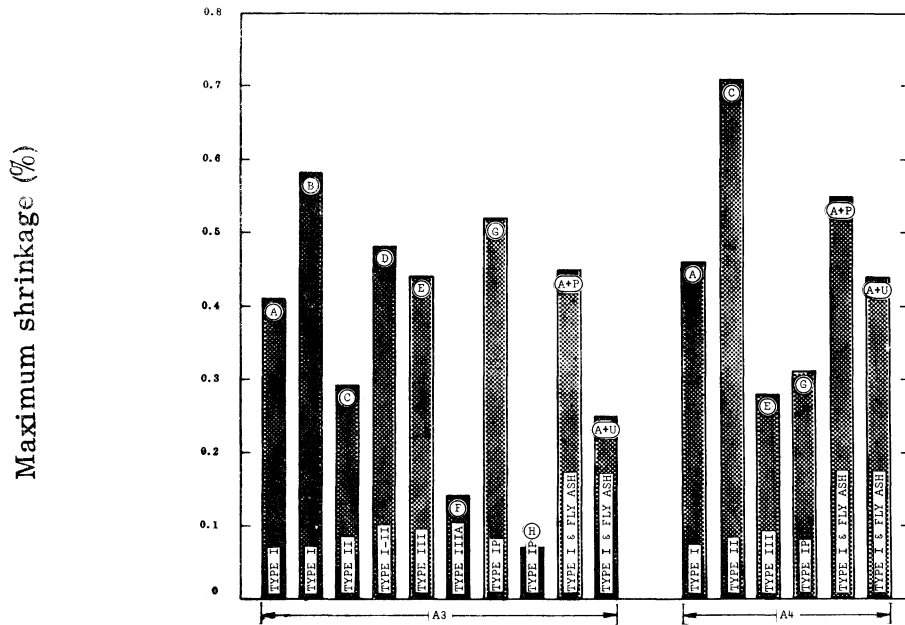


Figure 6. Maximum early volume change data.

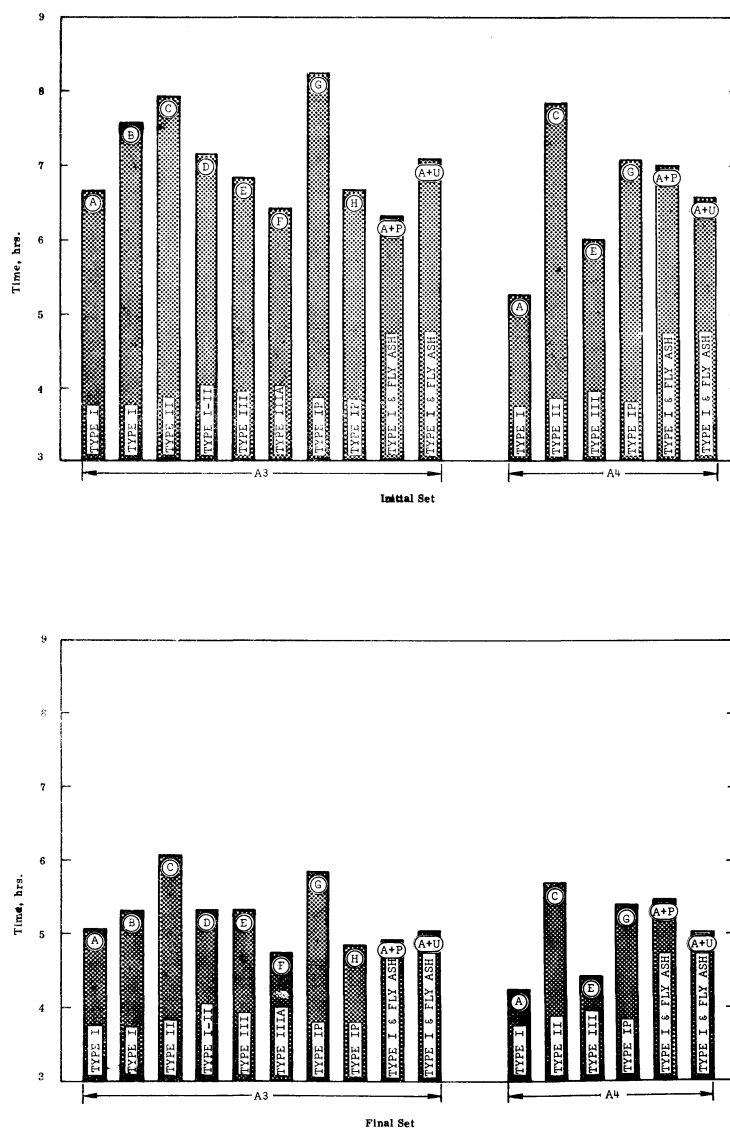


Figure 7. Time of set data.

Final Set

Type I cement with processed fly ash representing an A3 concrete reached the final set at the earliest time of 6 hours 20 minutes. An A3 mixture utilizing Type IP cement from source G had the latest time of 8 hours 15 minutes, 20 minutes slower than that with the Type II cement from source C. In A4 concretes, the earliest final set was attained by a Type I cement mixture at 5 hours 15 minutes, and the latest by a sample of a Type II cement mixture at 7 hours 50 minutes.

Heat of Hydration

The temperature levels reached during hydration of different types of cements, as well as a combination of Type I cement and fly ash, were observed by an adaptation of Method CRD-C 38-73 of the Corps of Engineers, Method of Test for Temperature Rise in Concrete. This method provides a procedure for measuring the temperature rise in concrete under adiabatic conditions caused by heat liberated from the hydration of cement. Cylinders measuring 6 x 12 in. (150 x 300 mm) were fabricated and located in well insulated autogenous curing containers to simulate the adiabatic conditions. To determine the temperature rise, one 20 gauge copper constantan thermocouple was inserted in the center of the cylinder to a depth of 6 in. (150 mm). Temperatures were plotted automatically for 48 hours at intervals of 1 hour on a 24 point automatic recorder.

A typical plot showing the relationship of temperature with respect to time is shown in Figure 8. The maximum temperatures reached are presented in Figure 9. In Appendix Table A-7 the data are summarized and the temperatures attained for certain time intervals are given. The maximum temperatures reached are also shown. The temperatures of fresh concrete mixtures varied from 70°F (21°C) to 78°F (26°C), and this variation may have had a slight influence on the rate of heat liberated.

In A3 mixtures, samples with Type IP cement from source H attained the lowest maximum temperature of 115°F (46.0°C) and the ones with Type III cement from source E the highest of 138°F (59.0°C). The lowest temperature in A4 concretes was reached by the specimens made with Type II cement at 124°F (51.0°C) and the highest temperature of 142°F (61.0°C) was reached by a Type III cement mixture. Samples incorporating fly ash and representing A4 concrete had higher temperature values than did Type II cement concrete, but gave lower values than Type I cement concrete. In A3 mixtures with fly ash, variable results, which generally reflect the moderate heat of hydration of fly ash, were observed. In the A4 mixtures, the level of maximum temperature and the rate of temperature increase were higher than for A3 concretes.

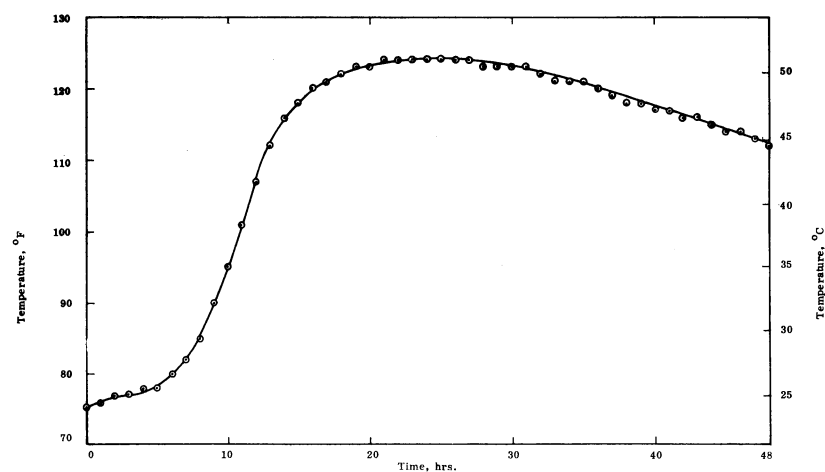


Figure 8. Typical curve showing the relationship of temperature with respect to time of autogeneously cured specimens. Data obtained from an A3 mixture containing Type II cement of source C.

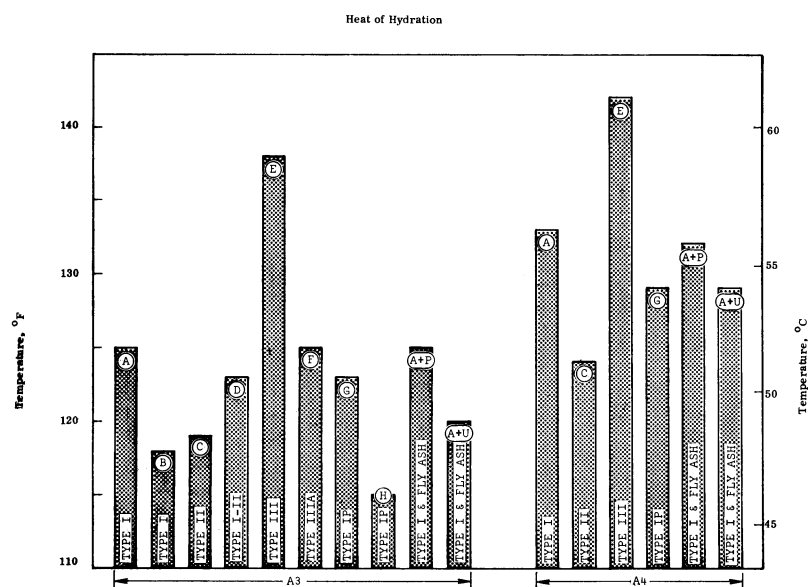


Figure 9. Maximum temperatures attained in autogeneously cured specimens.

CONCLUSIONS

1. Average 28-day flexural and compressive strengths of A3 mixtures incorporating fly ash at an optimum level were comparable to those of corresponding control Types I and II cement concretes. These strengths were lower but still satisfactory in A4 mixtures.
2. Average 28-day flexural and compressive strengths attained by concretes with IP cement and those containing fly ash were lower than the ones for the concretes with Type III cement from source E. Mixtures with Type IIIA cement from source F gave the lowest values among all the concretes.
3. Resistance to freezing and thawing in the presence of 2% NaCl caused more scaling on the specimens containing fly ash and IP cements than on the samples without fly ash. Specimens with lower water-cement ratios provided better scaling resistance.
4. Addition of fly ash to Type I cement mixtures lowered the maximum heat attained in autogenously cured specimens compared to corresponding control concretes since a lesser amount of cement was used. In A4 mixtures, higher maximum temperatures and a faster rate of temperature increase were observed as compared to the A3 mixtures.
5. Early shrinkage in mixtures incorporating fly ash was comparable to that for mixtures without fly ash. Mixtures with high cement contents in general yielded high early shrinkage.
6. Concretes made with Type IP and Type I cements and incorporating fly ash exhibited setting rates comparable to those of the control mixtures. It has been reported that fly ash possibly slows the setting time of cement; ⁽⁵⁾ however, such behavior cannot be concluded from this study.
7. Mixtures made with Type I cement and incorporating fly ash and those with Type IP cement required larger amounts of air entraining agent than did the control mixtures to attain the required range of air contents.
8. Type I mixtures utilizing fly ash and representing A3 concrete had slightly less water demand than did their control counterparts. However, in A4 mixtures the reverse was true. Type IP cement concrete required the same amount of water as did the control mixtures for A3 concretes but needed slightly more water in A4 mixtures than did the control mixtures.

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APPENDIX

TABLE A-1
Chemical and Physical Analyses of Cements Used

Properties	Cement Source								
Chemical: (%)	A	C	E	B	D	F*		H	G
SiO ₂	21.1	22.8	20.6	21.2	21.5	21.4			
Al ₂ O ₃	4.9	4.0	4.8	4.2	4.4	4.4			
Fe ₂ O ₃	2.5	3.6	2.4	3.3	3.3	3.1			
CaO	63.7	63.6	63.4						
MgO	3.5	3.0	3.3	4.3	3.6	3.6		2.8	1.1
SO ₃	2.6	2.6	3.3	2.7	2.7	2.8		1.6	2.6
Total Alkalies	0.73	0.60	0.75	0.65	0.71		0.67	0.68	0.63
C ₃ S	55.0	46.2	56.5	54	49	53			
C ₂ S	19.0	30.5	16.5						
C ₃ A	8.8	4.5	8.7	6	6	7			
Physical:									
Fineness (Blaine)	3470	3615	4695	3570	3620	5180	5135	3750	4522
Soundness (%)	0.11	0.11	0.05	0.13	0.08	0.08	0.05	0.03	
Time of Set: Vicat									
Initial (min) Gillmore	175	145	155				120	120	
Initial (hr: min)				1:50	1:55	2:05			2:35
Final (hr: min)				5:05	5:00	5:05			4:45
Compressive Strength (psi)**									
1-day	1895	1040	2575			2480	1805		
3-day	3165	2950	4385	3100	3250	3620	2655	3100	3410
7-day	4025	3750	4900	4000	4050		3075	3580	4610
Air Content (%)	10.2	10.1	11.2			19.4	17.0	5.9	4.6
Cement Type	I	II	III	I	I-II	IIIA	IIIA	IP	IP

* Values in the first column for cement source F were furnished by the manufacturer and those in the second column were determined by the Department

** 1 psi = 6.89 kPa 1000 psi = 6.89 MPa

TABLE A-2
Analyses of Processed and Unprocessed Fly Ash

Properties	Processed Fly Ash	Unprocessed Fly Ash
SiO ₂	55.50	53.38
Al ₂ O ₃	30.11	28.58
Fe ₂ O ₃	6.07	5.95
SO ₃	0.18	0.18
MgO	0.33	0.56
CaO	1.12	5.88
TiO ₂	1.10	0.60
Moisture	0.20	0.40
Loss on Ignition	3.38	2.45
% Retained on 325 mesh sieve	12.26	14.24
Specific Gravity	2.23	2.21

TABLE A-3
Air Content, Slump, and the Unit Weight Measurements of Samples Prepared from Different Types of Cement

Cement Type	Source	Class	Batch 1			Batch 2			Batch 3		
			Air, %	Slump, in.	Unit Wt. lb./ft. ³	Air, %	Slump, in.	Unit Wt. lb./ft. ³	Air, %	Slump, in.	Unit Wt. lb./ft. ³
I	A	A3	8.0	3.3	143.5	7.5	3.6	144.6	8.0	3.1	142.7
I	B	A3	5.7	3.7	145.0	6.9	4.4	142.1	7.5	3.8	143.9
II	C	A3	6.2	3.2	145.5	6.3	4.5	145.3	6.6	3.2	146.3
I-II	D	A3	6.6	4.0	144.5	5.8	4.8	145.1	6.5	3.0	145.5
III	E	A3	5.2	3.8	146.0	5.3	1.8	146.8	4.7	2.5	146.6
III A	F	A3	6.8	3.1	145.4	8.0	4.0	143.3	7.8	4.7	141.1
IP	G	A3	6.9	3.7	143.5	7.3	3.1	140.5	5.0	3.5	144.9
IP	H	A3	6.1	3.4	144.8	4.9	3.2	148.2	6.8	3.5	144.1
I & Ash	A & P	A3	7.1	3.0	142.1	7.5	3.5	142.0	5.7	3.2	145.6
I & Ash	A & U	A3	6.9	2.8	141.9	7.2	3.1	143.2	6.6	2.9	143.7
I	A	A4	5.7	3.0	146.5	5.3	2.5	147.8	6.9	3.0	145.2
II	C	A4	5.5	3.6	145.0	5.2	4.0	144.2	6.1	2.4	144.9
III	E	A4	6.8	2.7	144.5	5.6	3.0	147.2	5.4	3.3	146.8
IP	G	A4	6.7	3.1	143.3	6.3	2.7	141.1	7.1	3.0	143.1
I & Ash	A & P	A4	7.0	3.5	142.8	6.4	3.2	144.0	6.6	2.9	142.8
I & Ash	A & U	A4	7.2	2.4	144.0	5.1	3.3	143.7	5.3	2.2	146.0

P = Processed Fly Ash

U = Unprocessed Fly Ash

1 inch = 25 mm

1 lb./ft.³ = 16.0 kg/m³

TABLE A-4
Compressive and Flexural Strength Data
(Average of Three Specimens)

Cement Type	Source	Class	Compressive Strength in psi *			Flexural Strength in psi *		Ratio of Flexural to Compressive Strength	
			7 day	14 day	28 day	7 day	28 day	7 day	28 day
I	A	A3	3590	4290	4600	745	680**	0.21	0.15
I	B	A3	3700	4300	4940	645	755	0.17	0.15
II	C	A3	3600	4530	5390	625	790	0.17	0.15
I-II	D	A3	3780	4530	4950	630	710	0.18	0.14
III	E	A3	5010	5310	5730	745	795	0.15	0.14
III A	F	A3	3340	4020	4430	655	645	0.20	0.15
IP	G	A3	4110	4590	5000	600	710	0.15	0.14
IP	II	A3	4080	4690	5450	655***	690	0.16	0.13
I & Ash	A & P	A3	3670	4340**	4990**	685	710	0.19	0.14
I & Ash	A & U	A3	3710	4050	4830	635***	670***	0.17	0.14
I	A	A4	4640	5140	5460	760	735**	0.16	0.13
II	C	A4	4360	5090**	6000**	750***	785	0.17	0.13
III	E	A4	4770***	5270	5670	780	820**	0.16	0.14*
IP	G	A4	4530	4590	5130	645	680	0.14	0.13
I & Ash	A & P	A4	4100	4520**	5170**	650	720**	0.16	0.14
I & Ash	A & U	A4	3670	4220**	5200	505***	815***	0.14	0.16

P = Processed Fly Ash

U = Unprocessed Fly Ash

* 1 psi = 6.89 kPa 1000 psi = 6.89 MPa

** Average of two specimens

*** Single specimen

TABLE A-5

Early Volume Change Data taken at 50 Minute Intervals for 200 Minutes. Test started
13 Minutes after the Addition of Mixing Water

Cement Type	Source	SHRINKAGE, %				
		Class	50 Minutes	100 Minutes	150 Minutes	200 Minutes
I	A	A3	0.35	0.41	0.41	0.41
I	B	A3	0.42	0.53	0.57	0.58
II	C	A3	0.19	0.27	0.28	0.29
I-II	D	A3	0.35	0.47	0.48	0.48
III	E	A3	0.32	0.43	0.44	0.44
III A	F	A3	0.14	0.14	0.14	0.14
IP	G	A3	0.34	0.50	0.51	0.52
IP	H	A3	0.07	0.07	0.07	0.07
I & Ash	A & P	A3	0.31	0.44	0.45	0.45
I & Ash	A & U	A3	0.19	0.25	0.25	0.25
I	A	A4	0.28	0.45	0.46	0.46
II	C	A4	0.46	0.67	0.71	0.71
III	E	A4	0.22	0.27	0.28	0.28
IP	G	A4	0.28	0.31	0.31	0.31
I & Ash	A & P	A4	0.28	0.45	0.53	0.55
I & Ash	A & U	A4	0.26	0.40	0.44	0.44

P = Processed Fly Ash

U = Unprocessed Fly Ash

TABLE A-6
Time of Setting of Concrete Mixtures

Cement Type	Source	Class	Initial Set (hr:min)	Final Set (hr:min)
I	A	A3	5:05	6:40
I	B	A3	5:20	7:35
II	C	A3	6:05	7:55
I-II	D	A3	5:20	7:10
III	E	A3	5:20	6:50
III A	F	A3	4:45	6:25
IP	G	A3	5:50	8:15
IP	H	A3	4:50	6:40
I & Ash	A & P	A3	4:55	6:20
I & Ash	A & U	A3	5:05	7:05
I	A	A4	4:15	5:15
II	C	A4	5:40	7:50
III	E	A4	4:25	6:00
IP	G	A4	5:25	7:05
I & Ash	A & P	A4	5:30	7:00
I & Ash	A & U	A4	5:05	6:35

P = Processed Fly Ash

U = Unprocessed Fly Ash

TABLE A-7
Temperatures at Time Intervals up to 48 Hours in Autogenously Cured Specimens

Cement Type	Source	Class	Initial Temp. °F*	Temperature °F*							
				5 Hr.	10 Hr.	15 Hrs.	20 Hrs.	30 Hrs.	40 Hrs.	48 Hrs.	Max. Temp.
I	A	A3	72	83	113	124	125	119	112	107	125
I	B	A3	72	77	94	112	117	116	111	106	118
II	C	A3	70	75	89	110	116	119	114	109	119
I-II	D	A3	75	81	109	121	123	119	112	106	123
III	E	A3	74	83	118	137	138	129	119	113	138
III A	F	A3	75	87	117	124	125	118	111	106	125
IP	G	A3	75	85	104	120	123	119	113	109	123
IP	H	A3	70	75	93	110	115	114	109	106	115
I & Ash	A & P	A3	78	90	115	124	125	120	113	109	125
I & Ash	A & U	A3	74	82	108	116	119	117	111	107	120
I	A	A4	75	83	120	133	132	125	118	112	133
II	C	A4	75	78	95	118	123	123	118	112	124
III	E	A4	75	83	132	142	139	129	119	112	142
IP	G	A4	75	84	115	127	129	126	120	116	129
I & Ash	A & P	A4	78	91	126	132	132	125	118	112	132
I & Ash	A & U	A4	74	82	113	127	129	123	115	109	129

P = Processed Fly Ash

U = Unprocessed Fly Ash

* $t_c^0 = (t_F - 32) / 1.8$

