EFFECTS OF RETARDING ADMIXTURES ON PLASTIC
SHRINKAGE OF PORTLAND CEMENT PASTE

AUGUST 1973 - NUMBER 20

BY

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JHRP

JOINT HIGHWAY RESEARCH PROJECT
PURDUE UNIVERSITY AND
INDIANA STATE HIGHWAY COMMISSION

Interim Report
EFFECTS OF RETARDING ADMIXTURES ON PLASTIC SHRINKAGE
OF PORTLAND CEMENT PASTE

TO: J. F. McLaughlin, Director August 29, 1973
Joint Highway Research Project
FROM: H. L. Michael, Associate Director Project: C-36-47L
Joint Highway Research Project File: 5-6-12

The attached Interim Report covers a portion of the work performed on the HPR Part II Research Study titled "Effect of Retarders on Volume Changes in Portland Cement". This Report titled "Effects of Retarding Admixtures on Plastic Shrinkage of Portland Cement Paste", has been authored by Hanume Gowda under the direction of Professor C. F. Scholer.

The Report describes the effects of retarding admixtures, ASTM Type D, on plastic shrinkage of portland cement paste. The results indicate that plastic shrinkage, when using retarding admixtures, are higher than plastic shrinkage of plain paste. Evidence indicates that plastic shrinkage is influenced by the rate of evaporation, hydration and micro-structure of the paste.

The Interim Report is submitted as partial fulfillment of the objectives of the Study and for review and comment of the sponsors, the Indiana State Highway Commission and the Federal Highway Administration.

Respectfully submitted,

Harold L. Michael
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1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle EFFECTS OF RETARDING ADMIXTURES ON PLASTIC SHRINKAGE OF PORTLAND CEMENT PASTE		5. Report Date August 1973	
		6. Performing Organization Code C-36-47L	
7. Author(s) Hanume Gowda		8. Performing Organization Report No. JHRP-20-73	
9. Performing Organization Name and Address Joint Highway Research Project Civil Engineering Building Purdue University West Lafayette, Indiana 47907		10. Work Unit No.	
		11. Contract or Grant No. HPR-1(11) Part II	
12. Sponsoring Agency Name and Address* Indiana State Highway Commission 100 North Senate Avenue Indianapolis, Indiana 46204		13. Type of Report and Period Covered Interim Report	
		14. Sponsoring Agency Code CA 369	
15. Supplementary Notes Conducted in cooperation with the U.S. Department of Transportation, Federal Highway Administration. Research Study titled "Effect of Retarders on Volume Changes in Portland Cement Concrete".			
16. Abstract This paper describes the effects of water reducing and retarding admixtures, ASTM Type D, on plastic shrinkage of portland cement paste under different controlled relative humidities. Three types of commercial admixtures were used each representing a different common chemical classification of such retarders. Concentration of each retarder was that which gave fifty percent retardation of a 0.50 water-cement ratio mortar by penetration resistance. The length change measurements were made on thin cement paste sections floating on mercury. A magnetic proximeter was used to measure the length changes. The results of this work indicate that plastic shrinkages, when using retarding admixtures, are higher compared with the plastic shrinkage of plain paste. The higher shrinkage is due to the increased time in the plastic stage of paste and possible changes in paste microstructure evidenced by bleeding characteristics with some retarders. The appearance of plastic shrinkage cracks occurred during the transition from a high measured rate of shrinkage to a subsequent lower one. Evidence indicates that plastic shrinkage is influenced by the rate of evaporation, hydration and microstructure of the paste.			
17. Key Words Portland Cement Concrete, Cement Paste, Plastic Shrinkage, Plastic Drying Shrinkage, Admixtures		18. Distribution Statement	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 96	22. Price

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by

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Joint Highway Research Project

Project No.: C-36-47L

File No.: 5-6-12

Conducted by Purdue University
In Cooperation With The
Indiana State Highway Commission

Purdue University
West Lafayette, Indiana
August 29, 1973

ACKNOWLEDGEMENTS

The author is deeply grateful to Dr. C. F. Scholer, his major professor, for his kind guidance and encouragement during the course of this work. The help and valuable suggestions of Dr. W. L. Dolch and Dr. S. Diamond are most appreciated. Appreciation is also extended to Professor M. J. Gutzwiller.

The discussions with Mr. D. L. Gress and B. D. Barnes were helpful and meaningful in solving many difficulties.

This research was sponsored by the Indiana State Highway Commission and the Federal Highway Administration through the Purdue University Joint Highway Research Project. The author wishes to thank these organizations for their support of this work.

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TABLE OF CONTENTS

	Page
LIST OF TABLES	iv
LIST OF FIGURES	vi
ABSTRACT	viii
INTRODUCTION	1
Statement of the Problem	1
Review of Literature	2
Plastic Shrinkage and Plastic Shrinkage Cracking	2
Admixture	8
EXPERIMENTAL WORK	12
Materials	12
Retarding Admixtures	12
Cement	12
Water	16
Apparatus and Equipment	16
Procedure	23
Mixing the Cement Paste	23
Preparation of Specimen	23
Measurement of Plastic Shrinkage	24
RESULTS	27
Vicat Setting Times	27
Plastic Shrinkage	27
Analysis of Variance	44
DISCUSSION	54
Plastic Shrinkage	54
Plastic Shrinkage Cracking	59
CONCLUSIONS	64
LIST OF REFERENCES	65
APPENDIX	67

LIST OF TABLES

	Page
1. Retarding Admixtures	13
2. Chemical Properties of Cement, Lab. No. 319-1	14
3. Physical Properties of Cement, Lab. No. 319-1	15
4. Calibration of Systron Donner Voltmeter	21
5. Vicat Setting Times for Pastes	28
6. Shrinkage for Plain Paste at 25 Percent Relative Humidity	29
7. Shrinkage Using Lignosulfonate at 25 Percent Relative Humidity	30
8. Shrinkage Using Carbohydrate at 25 Percent Relative Humidity	31
9. Shrinkage Using Hydroxycarboxylic Acid at 25 Percent Relative Humidity	32
10. Shrinkage for Plain Paste at 50 Percent Relative Humidity	33
11. Shrinkage Using Lignosulfonate at 50 Percent Relative Humidity	34
12. Shrinkage Using Carbohydrate at 50 Percent Relative Humidity	35
13. Shrinkage Using Hydroxycarboxylic Acid at 50 Percent Relative Humidity	36
14. Shrinkage for Plain Paste at 75 Percent Relative Humidity	37
15. Shrinkage Using Lignosulfonate at 75 Percent Relative Humidity	38
16. Shrinkage Using Carbohydrate at 75 Percent Relative Humidity	39

LIST OF TABLES, cont.

	Page
17. Shrinkage Using Hydroxycarboxylic Acid at 75 Percent Relative Humidity	40
18. Equilibrium Shrinkages	49
19. F-Ratios for Linear Shrinkages	50
20. Slopes in the Straight Line Portion	52
21. F-Ratios for Slopes	53
Appendix	
Tables	
22. Comparison of Shrinkages at 25% R.H.	70
23. Comparison of Shrinkages at 50% R.H.	71
24. Comparison of Shrinkages at 75% R.H.	72
25. Shrinkages for Plain Paste	73
26. Shrinkages Using Lignosulfonate	74
27. Shrinkages Using Carbohydrate	75
28. Shrinkages Using Hydroxycarboxylic Acid	76
29. Comparison of Slopes at 25% R.H.	77
30. Comparison of Slopes at 50% R.H.	78
31. Comparison of Slopes at 75% R.H.	79
32. Slopes for Plain Paste	80
33. Slopes Using Lignosulfonate	81
34. Slopes Using Carbohydrate	82
35. Slopes Using Hydroxycarboxylic Acid	83
36. Nonevaporable Water Determination	84
37. Shrinkage of Plain Paste by Passing Laboratory Air Directly over the Specimen	85

LIST OF FIGURES

Figure	Page
1. Experimental Set Up for Shrinkage Measurement . . .	17
2. Sample Chamber	17
3. Top View of Sample Chamber	19
4. Calibration Set Up	19
5. Calibration of Systron Donner Voltmeter	22
6. Vapor Trap Bottles with Sulfuric Acid Solution . .	25
7. Arrangement of Probe and Steel Target when Measuring Length Change	25
8. Comparison of Shrinkages at 25% Relative Humidity .	41
9. Comparison of Shrinkages at 50% Relative Humidity .	42
10. Comparison of Shrinkages at 75% Relative Humidity .	43
11. Shrinkage Curves for Plain Paste	45
12. Shrinkage Curves Using (L), Lignosulfonate	46
13. Shrinkage Curves Using (S), Carbohydrate	47
14. Shrinkage Curves Using (A), Hydroxycarboxylic Acid.	48
15. Comparison of Specimens at 25% R.H.	62
16. Comparison of Specimens at 50% R.H.	63
Figures in Appendix	
17. Comparison of Specimens at Laboratory Condition . .	67
18. Shrinkage Curves Using Calcium Chloride	68
19. Comparison of Shrinkages at Laboratory Atmosphere .	69

ABSTRACT

Gowda, Hanume. M.S.C.E. Purdue University, August 1973.
Effects of Retarding Admixtures on Plastic Shrinkage of Portland
Cement Paste. Major Professor: C. F. Scholer

This paper describes the effects of retarding admixtures, ASTM Type D, on plastic shrinkage of portland cement paste. The length change measurements were made on a thin cement paste sections floating on the mercury. A magnetic proximeter was used to measure the length changes. In this work, the three types of commercial retarding admixtures that are chemically classified in the three principal categories were used. Concentration of each retarder was selected in such a way that it gave fifty percent of additional retardation compared with a control mortar by penetration resistance test. The water cement ratio used in the penetration resistance test on mortar was 0.50. In length change measurements of paste, a water cement ratio of 0.35 was used. The experiments were conducted at 25, 50 and 75 percent controlled relative humidities.

The plastic shrinkages of cement pastes with retarding admixtures were compared with the plastic shrinkage of plain paste. The appearance and amount of plastic shrinkage cracks were also compared.

The results of this work indicate that plastic shrinkages, when using retarding admixtures, are higher compared with the plastic shrinkage of plain paste. The higher shrinkage is due to the increased time

in the plastic stage of paste and possible changes in paste microstructure evidenced by bleeding characteristics with some retarders. The appearance of plastic shrinkage cracks occurred during the transition from a high measured rate of shrinkage to a subsequent lower one. Evidence indicates that plastic shrinkage is influenced by the rate of evaporation, hydration and microstructure of the paste.

INTRODUCTION

Statement of the Problem

The Indiana State Highway Standard Specifications, presently specifies the use of water-reducing retarding admixture as follows:

"Concrete used in the superstructure in structural steel and prestressed concrete spans shall contain a water-reducing retarding admixture when the superstructure contains members which are continuous over one or more piers or if it appears that the air or concrete temperature may exceed 70°F. during the pouring and finishing operations." (1)

Many properties of concrete are influenced in beneficial ways by the use of water-reducing retarding admixtures; however, greater plastic drying shrinkage may occur due to the increased length of time during which the concrete is in a plastic condition. When the concrete is restrained by foundations, steel reinforcements, etc. and with any volume change, stresses will develop that may rupture the concrete forming cracks. Tensile stress due to shrinkage is critical because the tensile strength of such young concrete is negligible. Plastic shrinkage of concrete is influenced by the rate of evaporation and presumably the response of cement paste to the evaporation as it undergoes hydration. Plastic shrinkage of neat cement paste is an indicator of the behavior of concrete containing such a paste (2).

The purpose of the proposed work is to determine the effects of retarders on plastic shrinkage of cement paste. Commercial admixtures, acceptable for use by Indiana State Highway Commission as water

reducing, retarding admixtures, conforming to ASTM C 494 type D specifications were considered (3). Three admixtures were selected which represented each of the three chemical classifications commonly found in commercial retarders:

1. lignosulfonic acids and their salts,
2. hydroxycarboxylic acids and their salts,
3. carbohydrates (sugars).

Review of Literature

Plastic Shrinkage and Plastic Shrinkage Cracking

"Volume decrease caused by drying and chemical changes" (14) which occurs after placement of the concrete and prior to attaining any significant strength is defined as plastic shrinkage. Lerch (4), explained the formation of plastic shrinkage cracks as follows:

"The disappearance of the sheen from the surface of the concrete indicates the time when the rate of evaporation exceeds the rate at which bleeding water rises to the surface. The time required to attain this condition will be influenced by the temperature, relative humidity, and wind velocity of the air and the temperature and bleeding characteristics of the concrete. At this stage the surface of the concrete has attained some initial rigidity; it cannot accommodate the rapid volume change of plastic shrinkage by plastic flow, and it has not developed sufficient strength to withstand tensile stress. Thus plastic shrinkage cracks may develop".

Plastic shrinkage is not objectionable unless it is accompanied by plastic shrinkage cracking (4). Usually the plastic shrinkage cracks are almost straight and do not have any definite symmetry or pattern; occasionally they have been observed in a crow-foot pattern.

They can be easily distinguished from other types of cracks by their depth and lack of pattern.

Plastic shrinkage cracks are not usually progressive (4). They develop prior to the time concrete hardens and they retain their original shape. However, the cracks increase in number and become wider after their initial appearance and before concrete hardens (5).

Plastic shrinkage cracks usually have considerable depth (4, 5). In pavement slabs, Lerch (4) found that the cracks have a depth of 4 inches. Sometimes the cracks will extend through the floor slab as well. Ravina and Shalon (5) observed that the cracks extending all the way through floor slabs can have a depth of 9 inches. They also measured the length and width of plastic shrinkage cracks of mortar exposed to different climatic conditions. The length varied from a few inches to a few feet and width varied from 0.004 inch to 0.12 inch.

To measure the shrinkage of cement paste, soon after mixing cement with water, Spindel (6) tried two different methods. The first one, involved placing the cement paste into a small glass bottle and closing with a watertight stopper. A capillary tube containing a short thread of colored liquid was inserted. The observed movement of the colored liquid showed the shrinkage of the cement paste. The second method consisted of measuring microscopically the distance between two points, initially 100 mm apart, fixed in a cement paste or mortar specimen.

From results of the above two experimental methods, Spindel (6) observed two critical points when shrinkage takes place; one near the initial setting time, and the other at the final setting time.

He also observed that the shrinkage measured during setting was often greater than that which occurred 24 or 48 hours after adding the water (according to the method ASTM C 157). Finally he concluded that the shrinkage during setting is most important.

Lerch (4) assumed that the rate of evaporation is the most important factor influencing plastic shrinkage and plastic shrinkage cracking. He also attributed the effects of temperature of air and concrete, relative humidity and wind velocity on the rate of evaporation. However, field investigation has shown that the bleeding characteristics of concrete do not have any major influence on plastic shrinkage and plastic shrinkage cracking. Attempts have been made to increase the bleeding rate of concrete by increasing the water cement ratio or by using different cements or aggregates, to eliminate plastic shrinkage cracking. These changes in the characteristics of concrete have not influenced plastic shrinkage and plastic shrinkage cracking.

Since the rate of evaporation from the surface is the most important factor for plastic shrinkage and plastic shrinkage cracking, precautions can be taken to minimize such shrinkage and shrinkage cracking. A slight change in atmospheric condition can produce a

considerable change in amount of plastic shrinkage and thereby in the extent of formation of plastic shrinkage cracks. Ravina and Shalon (5) measured the plastic shrinkage of mortar prisms starting from one hour after the beginning of mixing. They conducted tests on specimens of different mix proportions and exposed to different climatic conditions. The measured shrinkage values vary from 4000 to 11,000 millionths. Further, they measured evaporation of specimens exposed to different climatic conditions and found that values varied from 0.6 to 2.05 kg/m²/hour.

Slate and Matheus (7) measured the autogeneous volume change of cement paste and concrete starting from 15 minutes up to seven days after the addition of water. The volume change at seven days varied from 0.6 to 1.7 percent, with a decreasing rate of change throughout the period. In the case of cement paste, expansion was recorded up to 6 hours, followed by contraction.

The autogeneous volume changes measured by Slate and Matheus (7), closely agree with the results of del Campo (8). There is a difference between the results of the two studies; the initial expansion followed by contraction shown by Slate's and Matheu's results were not shown by del Campo's result. Slate and Matheus have not offered any explanation for this.

According to Beresford and Blakey (10), plastic shrinkage or prehardening cracks depend on differential settlement, rather than

on the magnitude or rate of bleeding. They also observed the phenomena of cracking within a few minutes of placement of concrete. In the case of fast bleeding, the cracks forming early, may disappear about the time the water leaves the surface, and reopen sometimes with subsequent rapid drying. When bleeding is long and slow, the early cracks are sharp and have less tendency to progress. Beresford and Blakey observed that the cracks resulting from rapid bleeding closed off easily at the top with delayed working of the concrete surface, and reopened if subsequent drying was rapid. The cracks always occur over reinforcement and over large pieces of aggregate or similar obstructions to settlement.

Tuthill (11) reported that plastic shrinkage cracks occurred on the surface of concrete footings even if the concrete was flooded with water immediately after placement. In his opinion, this type of cracking was not due to excessive drying. He also suggested that the false set due to a very low SO_3 content and other characteristics of cement may influence plastic shrinkage cracking.

Ravina and Sharon's (5) test results supported the fact that rapid evaporation has a predominant effect on plastic shrinkage cracking. Further, they observed that the appearance of plastic shrinkage cracks were consistently coincident with the transition from rapid volume change to the slow volume change. They suggested that this transition is due to changes in the flow properties of the mortar which in turn depend on the rate of hydration and to a lesser extent on evaporation. According to their test results no

correlation was found between the bleeding water and plastic shrinkage cracking. From the above discussion they concluded that plastic shrinkage cracking is not a direct function of shrinkage, water loss or evaporation rate. Also, they suggested that delayed stiffening of mortar by using slow setting cement or retarders, increases cracking when mortar is exposed to high evaporation due to the reduction of strength of mortar which is lower than the stress level caused by plastic shrinkage.

While discussing Lerch's paper Abdun-Nur (9) recommended the use of a water reducing retarding admixture to minimize plastic shrinkage cracking for the following reasons:

1. It delays the setting time, thereby keeping concrete in the plastic stage for a longer period. This aids it to adjust to volume changes due to drying, without developing cracks.
2. It keeps the rate of bleeding water greater than the rate of evaporation, thereby minimizing plastic shrinkage cracking.
3. It lowers the water cement ratio, which in turn decreases the potential volume change due to drying and therefore the potential shrinkage cracking.

Another advantage of using retarder is the gain in strength through lowered water cement ratio which results in improving the durability of concrete.

Abdun-Nur gave reasons to use water reducing retarding admixture, assuming that the rate of evaporation is the main predominant factor while causing plastic shrinkage cracking. But, he did not consider the effect of water reducing retarding admixture on the plastic shrinkage with the longer period of plastic stage of concrete. Hence, he was in disagreement with the findings previously discussed.

It seems that there are two schools of thought regarding the definition of plastic shrinkage and plastic shrinkage cracking, represented by Lerch on the one hand, and by Blakey, Beresford and Mattison on the other.

Lerch (4) concluded from his field studies that "if the rate of evaporation exceeds the rate at which bleeding water rises to the surface, then the plastic shrinkage and plastic shrinkage cracking are likely to occur." Blakey, Beresford and Mattison considered that the prime cause of the cracking is the settlement of the fresh concrete.

While analyzing the above studies, Ravina and Shalon (5), concluded that the plastic shrinkage cracks are the result of tensile stresses caused by shrinkage, and presetting cracks are the result of shear stresses caused by settlement. According to the above distinction, the present paper deals with plastic shrinkage and plastic shrinkage cracking only.

Admixtures

An admixture is defined as a material other than water, aggregates, and portland cement that is used as an ingredient of concrete and is

added to the batch immediately before or during its mixing. Additives are distinguished from admixtures as materials which are interground or interblended with portland cement during preparation rather than during mixing (12).

An admixture is used to modify the properties of concrete so that it is more suitable for the work at hand. The desired objectives may be achieved by changes in composition or proportions of the concrete mix rather than by the use of an admixture. Admixtures are no substitute for good concreting practices, but in certain instances, the desired objectives can be achieved economically by using suitable admixtures. Any admixture that is used should be employed only after appropriate evaluation of its effects with the particular concrete and under conditions of use intended. In considering the effects of admixtures on concrete it is pointed out by ACI Committee 212, Admixtures, (13) that:

1. A change in type of cement, amount of cement used, modification of aggregate, grading of mix proportions may be desirable.
2. Many admixtures affect more than one property of concrete, sometimes affecting desirable properties adversely.
3. The effects of some admixtures are significantly modified by such factors as wetness and richness of the mix, by aggregate grading and by character and length of mixing.
4. The specific effects of some admixtures vary with the type, quantity and properties of cement used.

5. Accordingly, some specific effects of an admixture usually can not be predicted accurately prior to testing.

ASTM designation C 494-71 defines type B and type D chemical admixtures as follows (3):

Type B- Retarding admixture: An admixture that retards the setting of concrete.

Type D- Water reducing and retarding admixtures: An admixture that reduces the quantity of mixing water required to produce concrete of a given consistency and retards the setting of concrete.

According to ASTM specification C 494 chemical admixtures meeting the requirements of type D will also meet the requirements for type B admixtures. Admixtures that are available for use as water reducing and set retarding concrete may be classified as follows:

1. Lignosulfonic acids and their salts.
2. Modifications and derivatives of lignosulfonic acids and their salts.
3. Hydroxylated carboxylic acids and their salts.
4. Modifications and derivatives of hydroxylated carboxylic acids and their salts.
5. Carbohydrates and modifications and derivatives thereof.

Classes 1 and 3 admixtures can be used either alone or in combination with other substances. They are water reducing and set retarding admixtures. Further, class 1 admixtures, lignosulfonic acids, entrain 2 to 6 percent air in the concrete, but class 3 admixtures,

hydroxylated carboxylic acid salts, act as water reducing, non-air entraining retarders.

Classes 2 and 4 are water reducing admixtures offered as combinations of substances designed to have varying degrees of acceleration or retardation in the rate of hardening of concrete.

Class 5 admixtures causes retardation of setting of portland cement and concrete when used alone. Many carbohydrates must be used with caution because widely varying retardation can be obtained with relatively small changes in proportions.

EXPERIMENTAL WORK

Materials

Retarding Admixtures

Three admixtures representing each of the three chemical classifications commonly found in commercial retarders were used:

1. lignosulfonic acids and their salts,
2. hydroxycarboxylic acids and their salts,
3. carbohydrates (sugar).

The concentrations of the three commercial retarding admixtures required for fifty percent retardation are determined by the penetration resistance test (ASTM C 403-70) on mortar with water cement ratio 0.50 by weight, concentration was expressed as weight percentage of the retardation solids based on the cement. This experimental work was carried out by Y. Yamamoto and details can be found in reference (17). Density, amount of solid content, and volume of solution required for 100 g of cement of each commercial retarder are shown in table 1.

Cement

The physical and chemical properties of the cement used are given in tables 2 and 3. The cement from a single mill grind was ASTM type I, Lab. No. 319-1. The cement, selected from one sack

TABLE 1 RETARDING ADMIXTURES

Type of Retarder	Density (g/cc)	Wt. of Residue Vol. of Liquid Admixture (g/cc)	% of Wt. of Residue by Wt. of Cement	Vol. of Liquid Admixture for 100g of Cement
Lignosulfonate	1.1472	0.37015	0.2600	0.70 cc
Carbohydrate	1.1518	0.41323	0.1000	0.24 cc
Hydroxycarboxylic Acid	1.1748	0.37654	0.0650	0.17 cc

TABLE 2 CHEMICAL PROPERTIES OF CEMENT, LAB. NO. 319-1.
(ASTM C 150)

Chemical Analysis

Compound	Percentage present
Silicon dioxide, SiO_2	21.64
Aluminum oxide, Al_2O_3	5.29
Ferric oxide, Fe_2O_3	2.19
Calcium oxide, CaO	65.36
Magnesium oxide, MgO	0.92
Sulfur trioxide, SO_3	2.40
Loss on ignition	1.89
Total alkalis, as Na_2O	0.35
Free lime	1.08
Insoluble residue	0.25

Potential Compound Composition

Compound	Percentage present
Tricalcium silicate, C_3S	56.03
Dicalcium silicate, C_2S	19.86
Tricalcium aluminate, C_3A	10.31
Tricalcium alumino ferrite, C_4AF	6.66
Calcium sulfate, CaSO_4	4.08

TABLE 3 PHYSICAL PROPERTIES OF CEMENT, LAB. NO. 319-1.
(ASTM C 150)

SETTING TIMES

Initial	2 hr. 55 min.
Final	4 hr. 15 min.
Vicat	1 hr. 55 min.

FINENESS

No. 325 sieve	93.7 percent
Wagner	1990 cm ² /g
Blaine	3870 cm ² /g

AIR CONTENT OF MORTAR 8.3 percent

EXPANSION 0.136 percent

TENSILE STRENGTH

One day	205 psi
Three days	345 psi
Seven days	430 psi
Twenty-eight days	520 psi

COMPRESSIVE STRENGTH

One day	1550 psi
Three days	3130 psi
Seven days	4600 psi
Twenty-eight days	6450 psi

only, was sieved through No. 50 sieve and stored in sealed glass bottles before using.

Water

For preparation of cement paste, deionized water was used for mix water.

Apparatus and Equipment

An apparatus designed to measure plastic shrinkage of cement paste has been described by Cromarty and Bryden (16). In designing their apparatus they considered the effect of restraint between the specimen and its support, and the effect of size of the specimen. They used a mercury bed to reduce the effect of restraint, and a gage length of 5 in (12.7 cm) to secure the desired accuracy of the measurement of length changes. The same concept was used by Orr, Mice and Haigh (15), who used a gage length of 15 cm, to permit measurement of the larger strains which are associated with conditions under which the plastic shrinkage cracking is likely to occur. In the present work also, a gage length of 15 cm was used.

The general arrangement of the apparatus and other necessary equipment required is shown in Figure 1. The apparatus, built of plexiglass, rests on an aluminum plate 62 cm long, 27 cm wide and 2.5 cm thick. Three foot screws are provided to level the mercury in the tank. The main apparatus with the base plate is shown in Figure 2. Specimens with a gage length of 15 cm and a cross-section of 2.5 cm by 0.65 cm were chosen. A small box in the main apparatus,

FIGURE 1 EXPERIMENTAL SET UP FOR SHRINKAGE MEASUREMENT

FIGURE 2 SAMPLE CHAMBER

measuring 38.5 cm long, 11 cm wide and 6.5 cm high, was chosen to contain the specimen while measuring plastic shrinkage. The shape of the specimen is shown in Figure 3. The top plate for the box is provided with screws so that after casting the specimen, the box can be made air tight. The mold for the specimen on the mercury bed (0.65 cm thick) is as shown in Figure 3. One end of the specimen is attached to the fixed head; the other end to the movable head. The straight portion of the specimen in between the movable and fixed heads is taken as the gage length. The fixed head is attached to the sides of the box leaving 0.65 cm from the bottom. The movable head and the specimen were allowed to float on the mercury bed, which was provided to reduce the restraining effect of the bottom surface of the specimen when it shrinks.

To measure the changes in length of the specimen, the previous investigators (15, 16) used an LVDT (Linear Variable Differential Transformer). In this present work a magnetic proximeter, Bently Nevada, model No. 3115 and a probe model No. 308L 18 were used for simplicity and the elimination of frictional resistance. The magnetic proximeter, the probe, the voltage regulator and the digital voltmeter with micrometer are shown in Figure 4. In this figure the probe is fixed in position in front of the micrometer. After placing the steel target, with a thickness of 0.004 inch, in position in front of micrometer, the set up shown in Figure 4 was used to get the calibration curve. This is a curve of output voltage versus the gap between probe and steel target. While measuring the length changes of a

FIGURE 3 TOP VIEW OF SAMPLE CHAMBER

1 Movable head	2 Fixed head
3 Specimen	4 Probe

FIGURE 4 CALIBRATION SET UP

specimen, the steel target was positioned at the gage point (near the movable head), and the probe was fixed in front of steel target. The voltage regulator was used to regulate an input voltage of minus 18 volts which was required for the proximeter. After completing connections, the voltage in the digital voltmeter is the function of distance between the steel target and the probe.

The calibration curve (Figure 5) was prepared by using a micrometer having a least count of 0.0001 in. The steel target was positioned on the front of the micrometer, which was fixed to the vertical plexiglass stand prepared for this purpose. The probe was fixed in another vertical stand in front of the steel target, and the other end of the probe was connected to the proximeter. Before connecting the probe a minus 18 volt input voltage to the proximeter was obtained with the help of the voltage regulator. Starting from zero reading in the voltmeter, the steel target almost touching the probe front face, the micrometer was adjusted to read zero. The micrometer was then repeatedly turned back, that is the gap between the probe and the steel target was increased repeatedly by increments of 0.0005 in, and the corresponding output voltage readings were taken. The voltmeter readings in volts versus the measured gap between the steel target and probe were then plotted.

To maintain the relative humidity constant, air was passed through vapor trap bottles containing sulfuric acid of the correct dilution to produce the desired relative humidity, and then over the specimen. The sulfuric acid solution was adjusted for the desired relative humidity by measuring and acid adjusting its density according

TABLE 4 CALIBRATION OF SYSTRON DONNER VOLTMETER

Micrometer Reading (inch)	Voltmeter Reading (volts)	Micrometer Reading (inch)	Voltmeter Reading (volts)
0.000	0.000	0.100	5.620
0.005	0.116	0.105	5.977
0.010	0.326	0.110	6.340
0.015	0.535	0.115	6.702
0.020	0.737	0.120	7.034
0.025	0.943	0.125	7.317
0.030	1.202	0.130	7.642
0.035	1.476	0.135	7.965
0.040	1.755	0.140	8.292
0.045	2.023	0.145	8.586
0.050	2.280	0.150	8.822
0.055	2.600	0.155	9.100
0.060	2.937	0.160	9.379
0.065	3.272	0.165	9.648
0.070	3.587	0.170	9.887
0.075	3.884	0.175	10.08
0.080	4.438	0.180	10.30
0.085	4.607	0.185	10.52
0.090	4.976	0.190	10.72
0.095	5.316	0.195	10.91

FIGURE 5 - CALIBRATION OF SYSTRON DONNER VOLTMETER.

to ASTM E 104-51. Figure 6 illustrates the vapor trap bottles. Constant flow was maintained with the aid of a water manometer by keeping a one cm constant head. An aspirator was used to draw the air through sulfuric acid solution. The relative humidities obtained were verified by using a relative humidity sensor, placed inside the sample container. A thermometer was inserted from the top of the box to record the temperature during the experiment.

Procedure

Mixing the Cement Paste

115 g of cement was weighed using a triple beam balance, and transferred to a friction top can. A new can was used for each mix. When using a retarding admixture, a stock solution of the admixture sufficient for five experiments and fifty percent retardation was prepared. The prepared solution was used within a week after preparation. The solution required for a water cement ratio of 0.35 by weight was then measured by graduated cylinder and added to the cement. Using a mechanical paint mixer, the cement and water were mixed for two minutes. As soon as the mixing period was over the can was opened and again mixed with a steel spoon to make sure the paste was mixed completely.

Preparation of the Specimen

The specimen was cast on a mercury bed by placing two straight plexiglass form pieces with a thickness of 0.65 cm, between the movable

and fixed heads. While casting the specimen an 0.004 in. thick steel target was positioned at the gage point near the movable head. The specimen was levelled to the surface of the side plexiglass form pieces. The probe was fixed in front of the steel target and connected to the proximeter. Figure 7 illustrates the arrangement of the probe. After casting, the side plexiglass pieces were removed carefully without disturbing the specimen. The top plate was screwed tight to the box and the joints around it sealed with electric tape to make the chamber air tight.

Air drawn through the sulfuric acid solution was allowed to pass over the specimen, and the amount of flow was controlled by keeping a one cm head of water in the water manometer. With the help of the voltage regulator, a minus 18 volts reading was secured as the input voltages to the proximeter. The first reading was taken after connecting the probe to the proximeter. The time elapsed between the water added and the first reading taken was maintained as 20 minutes for all experiments. For the purpose of calculation, the time of first reading taken was considered to be zero. Up to the equilibrium shrinkage stage voltmeter readings were recorded. For the calculation of shrinkage the distance between the movable and fixed heads was considered as the gage length and was 15 cm (5.9 inches).

Measurement of Plastic Shrinkage

Following the procedures previously presented, voltmeter readings for each experiment were recorded periodically to determine the change

FIGURE 6 VAPOR TRAP BOTTLES WITH SULFURIC ACID SOLUTION

FIGURE 7 ARRANGEMENT OF PROBE AND STEEL TARGET WHEN MEASURING LENGTH CHANGE

in gap between the probe and the steel target resulting from shrinkage. From the calibration curve for the change of voltage, the corresponding change in probe gap which is equivalent to the linear deformation was calculated. By using a gage length of 15 cm (5.9 inches) the shrinkage strains in millionths were calculated and tabulated.

RESULTS

Vicat Setting Times

Vicat setting times for pastes made with water cement ratio 0.35 by weight are tabulated in the Table 5. Vicat setting times were determined for both plain paste and paste containing retarding admixtures. The procedure for conducting the Vicat setting time experiment was followed according to the ASTM C 191-71. It should be noted that the different water cement ratios were used in the penetration resistance test and in the Vicat setting time experiment. In the penetration resistance test, mortar of water cement ratio 0.50 by weight was used. Vicat setting times were determined on cement pastes of water cement ratio 0.35 by weight, since this water cement ratio was used in the plastic shrinkage experiments.

Plastic Shrinkage

Measurements of the plastic shrinkage of plain and retarded portland cement pastes were carried out at three different relative humidities, 25, 50 and 75 percent. In Tables 6 - 17, the measured voltage, which is a function of distance between the probe and steel target, and the calculated linear shrinkage in millionths, are tabulated. Voltage readings were recorded until their change was negligible i.e. shrinkage ceased. A sample calculation is given in the Appendix.

TABLE 5 VICAT SETTING TIMES FOR PASTES

Description of Paste	Water:Cement Ratio by Wt.	Vol of Liquid Admixture for 100 g of Cement	Vicat Setting Times
Plain	0.35	--	215 min.
With Ligno-sulfonate	0.35	0.70 cc	360 min.
With Carbo-hydrate	0.35	0.24 cc	370 min.
With Hydroxy-carboxylic Acid	0.35	0.17 cc	305 min.

Figures 8, 9 and 10 are the plots of linear shrinkage in percent versus time in hours at different relative humidities. The initial expansion recorded was followed by contraction in all cases. The initial expansion was probably due to the formation of ettringite in the paste. This early expansion is more predominant in plain paste as compared to the pastes with the retarders. When retarders were used, a higher rate of shrinkage soon overshadows the initial expansion. As the initial stiffening of cement paste increases, shrinkage increases at a constant rate. The slope of the curve and ending of linearity are different for different curves.

In the Figure 9, the initial expansion in the case of plain paste is noticeable compared to the other three curves. The rate of shrinkage (the slope) is same for both plain pastes and those made with hydroxycarboxylic acid. A different and slightly lower rate of

TABLE 6 SHRINKAGE FOR PLAIN PASTE AT 25 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Average Temp. During Expt. = 25.5°C	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 25.0°C	Voltmeter Reading (volts)	Linear Shrinkage (millionths)
0	2.165	--	--	2.226	--	--
$\frac{1}{2}$	2.196	170	--	2.237	85	128
$1\frac{1}{2}$	2.567	1187	--	2.587	1017	1102
$2\frac{1}{2}$	2.896	2034	--	3.028	2034	2034
$3\frac{1}{2}$	3.136	2628	--	3.282	2712	2670
$4\frac{1}{2}$	3.272	2967	--	--	--	--
5	--	--	--	3.374	2967	2986*
$5\frac{1}{2}$	3.292	3051	--	---	--	--
6	3.294	3051	--	--	--	3009*
$6\frac{1}{2}$	--	--	--	3.376	2967	--

* By interpolation

TABLE 7 SHRINKAGE USING LIGNOSULFONATE AT 25 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Average Temp. During Expt. = 27.0°C			Average Temp. During Expt. = 27.0°C		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)		Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Linear Shrinkage (millionths)
0	1.870	--		1.860	--	--
1	2.008	339		1.940	170	255
2	2.266	1102		2.232	1017	1060
3	2.532	1950		2.520	1950	1950
4	2.870	2712		2.808	2628	2670
5½	3.134	3475		3.089	3390	3433
6½	3.189	3644		3.123	3560	3602
7	3.192	3644		3.142	3560	3602

TABLE 8 SHRINKAGE USING CARBOHYDRATE AT 25 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 27.0°C	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 27.0°C
0	2.088	--		1.887	--	--
1	2.148	170		1.954	85	126
2	2.450	1017		2.245	1017	1017
3	2.857	2119		2.638	2119	2119
4	3.218	2967		2.960	2882	2925
5	3.617	3983		3.346	3899	3941
6	3.903	4831		3.627	4661	4746
7	3.956	4916		3.678	4746	4831

TABLE 9 SHRINKAGE USING HYDROXYCARBOXYLIC ACID AT 25 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 27.0°C	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 27.0°C
0	1.900	--	--	2.120	--	--
1	2.088	594		2.308	594	594
2	2.404	1441		2.490	1272	1357
3½	3.080	3305		3.088	3051	3178
5	3.876	5255		3.866	4831	5043
6	4.187	6102		4.246	5678	5890
7	4.221	6187		4.286	5848	6018

TABLE 10 SHRINKAGE FOR PLAIN PASTE AT 50 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1 Average Temp. During Expt. = 26.5°C			Experiment No. 2 Average Temp. During Expt. = 26.5°C		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Linear Shrinkage (millionths)	
0	2.352	--	2.460	--	--	--
1	2.388	85	2.502	85	85	85
2	2.707	847	2.808	932	890	890
3	3.032	1695	3.106	1695	1695	1695
4	3.260	2288	3.288	2203	2246	2246
5	3.326	2458	3.340	2373	2416	2416
6	3.334	2542	3.352	2458	2500	2500

TABLE 11 SHRINKAGE USING LIGNOSULFONATE AT 50 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Average Temp. During Expt. = 27.0°C	Linear Shrinkage (millionths)	Voltmeter Reading (volts)	Average Temp During Expt. = 27.0°C	Linear Shrinkage (millionths)	Average Linear Shrinkage (millionths)
0	1.810	--	1.821	--	--	--
1	1.915	339	1.966	339	339	339
2	2.092	848	2.150	933	933	891
3	2.292	1526	2.312	1441	1441	1484
4½	2.562	2289	2.592	2289	2289	2289
6	2.866	3051	2.844	2967	2967	3009
7½	2.941	3221	2.964	3136	3136	3179

TABLE 12 SHRINKAGE USING CARBOHYDRATE AT 50 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Average Temp. During Expt. = 26.5°C			Average Temp. During Expt. 26.5°C		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Linear Shrinkage (millionths)	
0	1.930	--	1.840	---	--	
1	2.025	339	1.972	339	339	
2	2.262	932	2.174	1017	975	
3	2.397	1441	2.326	1441	1441	
4½	2.603	2034	2.512	1950	1992	
6	2.925	2882	2.804	2797	2840	
7½	3.208	3560	3.106	3475	3518	
8½	3.246	3644	3.156	3644	3644	

TABLE 13 SHRINKAGE USING HYDROXYCARBOXYLIC ACID AT 50 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1		Experiment No. 2		Average Linear Shrinkage (millionths)
	Average Temp. During Expt. = 28.0°C		Average Temp. During Expt. = 28.0°C		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	
0	1.753	--	1.725	--	--
1	1.923	594	1.932	678	636
2	2.278	1610	2.258	1695	1663
3	2.522	2288	2.552	2458	2373
4	2.762	2967	--	--	--
4½	--	--	2.878	3390	3345*
5	3.031	3644	--	--	--
6	3.335	4407	3.360	4492	4450
7	3.394	4662	--	--	--
7½	--	--	3.436	4746	4700*
8	3.452	4746	3.442	4831	4789

* By interpolation

TABLE 14 SHRINKAGE FOR PLAIN PASTE AT 75 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 25.5°C	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 25.5°C
0	2.096	--		2.185	--	--
1	2.077	0		2.130	0	0
2	2.190	339		2.272	255	297
3	2.337	678		2.418	594	636
4½	2.500	1187		2.593	1102	1145
6	2.540	1356		2.635	1272	1314
7½	2.547	1356		2.642	1272	1314

TABLE 15 SHRINKAGE USING LIGNOSULFONATE AT 75 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 26.0°C	Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Temp. During Expt. = 26.0°C
0	1.830	--		1.882	--	--
1	1.876	85		1.905	85	85
2	2.040	678		2.009	424	551
3	2.175	1017		2.119	848	933
4½	2.424	1780		2.361	1526	1653
6	2.650	2458		2.580	2204	2331
7½	2.735	2543		2.705	2458	2500

TABLE 16 SHRINKAGE USING CARBOHYDRATE AT 75 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Average Temp. During Expt. = 25.5°C			Average Temp. During Expt. = 25.5°C		
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)		Voltmeter Reading (volts)	Linear Shrinkage (millionths)	Average Linear Shrinkage (millionths)
0	2.226	--		1.944	--	--
1	2.260	170		2.116	424	297
2	2.394	509		2.265	848	679
3	2.495	848		2.378	1187	1018
4½	2.662	1272		2.525	1611	1442
6	2.812	1695		2.652	2034	1865
7½	2.996	2204		2.820	2373	2289

TABLE 17 SHRINKAGE USING HYDROXYCARBOXYLIC ACID AT 75 PERCENT RELATIVE HUMIDITY

Water:Cement Ratio = 0.35

Time (hours)	Experiment No. 1			Experiment No. 2		
	Average Temp. During		Average Temp. During Expt. = 25.0°C	Average Temp. During		Average Temp. During Expt. = 25.0°C
	Voltmeter Reading (volts)	Linear Shrinkage (millionths)		Voltmeter Reading (volts)	Linear Shrinkage (millionths)	
0	1.980	--		2.075	--	--
1	2.118	424		2.250	509	467
2	2.280	848		2.485	1102	975
3	2.400	1187		2.628	1441	1314
4	2.510	1611		2.798	1780	1695
5½	2.700	2289		2.956	2289	2289
7	3.010	2797		--	--	--
8½	3.137	3136		3.142	2967	3052

FIGURE 8 -COMPARISON OF SHRINKAGE AT 25% RELATIVE HUMIDITY.

FIGURE 9 - COMPARISON OF SHRINKAGES AT 50% RELATIVE HUMIDITY.

FIGURE 10 - COMPARISON OF SHRINKAGES AT 75% RELATIVE HUMIDITY.

shrinkage is observed for pastes made with either lignosulfonate or carbohydrate retarders.

Figures 11, 12, 13 and 14 show the linear shrinkage versus time for plain paste and paste with retarding admixtures.

Analysis of Variance

An analysis of variance was conducted on the results of the equilibrium shrinkages of plain paste and paste with retarding admixtures, in an effort to test whether they significantly differ or not at the one percent level. The 'F' test, or variance ratio test, was used to make comparisons. Contrasts were constructed, plain paste versus paste with each retarding admixture, and within a particular type, for experiments at one relative humidity versus the other.

Equilibrium shrinkages are tabulated in the Table 18. The equilibrium shrinkages are those existing when the change in shrinkage becomes negligible. The 'F' ratios for the comparisons between plain paste and pastes with different types of retarding admixtures are tabulated in the Table 19. Table 19 also shows the 'F' ratios for comparisons at different relative humidities.

For the equilibrium shrinkage of plain paste compared with that of different type of retarding admixtures, the 'F' ratios are significantly different at the one percent level. This is true at all relative humidities, except for plain paste versus lignosulfonate at

FIGURE II - SHRINKAGE CURVES FOR PLAIN PASTE .

FIGURE 12 - SHRINKAGE CURVES USING (L), LIGNOSULFONATE.

FIGURE 13 - SHRINKAGE CURVES USING (S), CARBOHYDRATE.

FIGURE 14 - SHRINKAGE CURVES USING (A), HYDROXY CARBOXYLIC ACID.

TABLE 18 EQUILIBRIUM SHRINKAGES
(millionths)

R.H.	Plain Paste	Paste with Lignosulfonate	Paste with Carbohydrate	Paste with Hydroxycar- boxylic Acid
25%	3051	3644	4916	6187
	2967	3560	4746	5848
50%	2542	3221	3644	4746
	2458	3136	3644	4831
75%	1356	2543	2204	3136
	1272	2458	2373	2967

TABLE 19 F-RATIOS FOR LINEAR SHRINKAGE

Source	R. H.=25%	R. H.=50%	R. H.=75%
Overall	F=181.3 Significant	F=689.7 Significant	F=117.7 Significant
Plain Paste versus Lignosulfonate	F= 17.8 Not Significant	F=171.2 Significant	F=157.7 Significant
Plain Paste versus Carbohydrate	F=168.1 Significant	F=486.8 Significant	F=106.4 Significant
Plain Paste versus Hydroxycarboxylic Acid	F=458.4 Significant	F=1948.2 Significant	F=338.2 Significant
Source	Plain Paste	Using Lignosulfonate	Using Carbohydrate
Overall	F=428.8 Significant	F=172.2 Significant	F=337.9 Significant
25% R.H. Vs 50% R.H.	F=73.4 Significant	F=50.0 Significant	F=147.1 Significant
50% R.H. Vs 75% R.H.	F=398.7 Significant	F=128.2 Significant	F=191.8 Significant
			F=176.8 Significant
			F=60.1 Significant
			F=120.1 Significant
			F=176.8 Significant
			F=60.1 Significant
			F=120.1 Significant

25 percent relative humidity. As expected, the 'F' ratios are significantly different for each of the types when compared at different relative humidities.

An analysis of variance was also conducted for the slopes of the curves in the region where the rate of shrinkage was considerable. The slopes of each curve was calculated by fitting a straight line using the method of least squares for the region where the rate of shrinkage was considerable. Then the same kind of procedure was followed as explained before.

The slopes are tabulated in the Table 20 for plain paste and pastes with retarding admixtures at different relative humidities. The 'F' ratios are tabulated in Table 21. As expected, the 'F' ratios are significantly different within each type for comparisons at different relative humidities except for the comparison of plain paste at 25 percent relative humidity versus plain paste at 50 percent relative humidity. The 'F' ratios of the slopes of the straight line regions are compared for plain paste and pastes with retarding admixtures at different relative humidities.

TABLE 20 SLOPES* IN THE STRAIGHT LINE PORTION

R.H.	Plain Paste	Paste with Lignosulfonate	Paste with Carbohydrate	Paste with Hydroxycarboxylic Acid
25%	822.1	709.9	944.3	1021.6
	889.8	723.8	922.5	959.5
50%	711.1	547.1	468.6	725.7
	745.7	527.3	490.9	750.6
75%	339.1	429.1	303.5	400.3
	318.4	467.8	315.9	361.1

* $\text{Slope} = \frac{\text{Difference of Shrinkages in millionths}}{\text{Difference of times in hours}}$

TABLE 21 F-RATIOS FOR SLOPES

Source	R.H.=25%	R.H.=50%	R.H.=75%
Overall	F=24.67 Significant	F=103.05 Significant	F=17.08 Significant
Plain Paste versus Lignosulfonate	F=16.9 Not Significant	F=108.1 Significant	F=31.7 Significant
Plain Paste versus Carbohydrate	F=5.27 Not Significant	F=182.9 Significant	F=0.8 Not Significant
Plain Paste versus Hydroxycarboxylic Acid	F=15.9 Not Significant	F=0.28 Not Significant	F= 5.9 Not Significant
Source	Plain Paste	Using Lignosulfonate	Using Carbohydrate
Overall	F=146.2 Significant	F=108.4 Significant	F=1109.42 Significant F=187.3 Significant
25% R.H. Vs 50% R.H.	F=15.7 Not Significant	F=93.5 Significant	F=1098.42 Significant F=63.5 Significant
50% R.H. Vs 75% R.H.	F=155.4 Significant	F=22.8 Not Significant	F=154.35 Significant F=127.4 Significant
			Using Hydroxy-carboxylic Acid

DISCUSSION

Plastic Shrinkage

Figures 8, 9 and 10 show linear plastic shrinkages in percent for the plain paste and pastes with retarding admixtures at three different relative humidities. At the three different relative humidities, the plastic shrinkages measured for pastes with retarding admixtures are higher than plastic shrinkage for the plain paste. An initial expansion, followed by rapid contraction was measured in all the cases. This initial expansion was probably due to the formation of ettringite in the paste.

Figure 9 shows that transitions from rapid plastic shrinkage to slow shrinkage were different for different pastes. This transition for plain paste occurs at about 4 hours, and for pastes with retarding admixtures at about 6 hours after the commencement of the experiment. The Vicat initial setting times for the plain paste and pastes with retarding admixtures are $3\frac{1}{2}$ hours and 6 hours respectively, except that the paste made with hydroxycarboxylic acid retarder has an earlier initial setting time than the other admixtures. When retarding admixtures were used, it was very difficult to locate the transition between rapid shrinkage and slow shrinkage so the stated transition may be off by one hour from the above stated value (6 hours) depending on ones interpretation of the curve.

It is recalled that the dosages of retarding admixtures used were the dosages required for fifty percent retardation determined by the penetration resistance test. This test was carried out with mortar of water cement ratio 0.50 by weight. In contrast, the Vicat initial setting times were determined for pastes with water cement ratio 0.35 by weight. It was observed that in determining the Vicat initial setting times and in casting specimens in the shrinkage experiments, the amount of bleeding water available to evaporate from the surface when hydroxycarboxylic acid was used, was much greater than that with the other two types of retarding admixtures and for plain paste. In consequence of the high rate of bleeding a lower effective water cement ratio resulted, hence reducing the initial setting time compared with the other two types of retarding admixtures. The above discussion is not necessarily true in a penetration resistance test on a larger specimen such as used for the penetration tests by Yamamoto as previously mentioned.

The plastic shrinkages for the pastes with carbohydrate and lignosulfonate were higher than the plastic shrinkage for the plain paste. This apparently was due to the increased time in which these pastes were in the plastic stage. Rates of shrinkage (slopes) for pastes with lignosulfonate and carbohydrate differ significantly from the rate of shrinkage of plain paste. When lignosulfonate or carbohydrate was used, it was observed that less bleeding occurred than for plain paste.

The plastic shrinkage for paste with hydroxycarboxylic acid retarder was higher than the plastic shrinkages of the other two types of retarders. Also as seen in Figure 9, the rate of shrinkage with hydroxycarboxylic acid retarder was higher than the rate of shrinkages of the other two types of retarders. This was accompanied by an observed high rate of bleeding. High rates of shrinkage were therefore associated with the bleeding of plain paste and pastes with type D admixtures which exhibited bleeding.

Referring to the results of the analysis of variance, Table 19, the above discussion, i.e. admixtures cause greater shrinkages, was shown true at all relative humidities except for plain paste versus lignosulfonate at 25 percent relative humidity. In the case of lignosulfonate it was not significantly different from plain paste at the 25 percent relative humidity yet it was significant at both 50 and 75 percent humidities. Further comparison of its performance shows that it was less sensitive to humidity conditions. For example referring to Figure 10, at 75 percent relative humidity lignosulfonate paste is second highest in shrinkage. Yet at 25 percent relative humidity, see Figure 8, it is only slightly higher than plain paste (and not statically different) while other admixtures have a much greater increase in shrinkage at the lower relative humidity. This indicates that under variable conditions of humidity, such as experienced in field concreting practice, lignosulfonate admixture will produce a more uniform product with respect to plastic shrinkage.

Paste with retarding admixtures gave higher shrinkages than the plain paste. This was in part due to the retardation in setting time. An experimental run was conducted with calcium chloride (2 percent by weight of cement) as an accelerator at each of the three humidities to reduce the setting below that of plain paste. Due to the decreased time in which the paste was in the plastic stage, the plastic shrinkage was expected to be less than for plain paste. The results show, in Figure 18 (Appendix), when compared to the plain paste of Figure 11, that this did in fact occur. However, the rate of shrinkage (slope) obviously is greatest for the calcium chloride. This also is evident in Figure 19. For the condition measured calcium chloride resulted in decreased total plastic shrinkage.

Figure 19 (Appendix) shows the plot of linear shrinkage open to the laboratory atmosphere. Under this condition shrinkages were greater as compared with controlled relative humidity conditions. The relative humidity of the laboratory was approximately 50 percent. It was suspected that the rate of evaporation in an open atmosphere was higher than the rate of evaporation in controlled relative humidity condition. When the rate of evaporation was more, the water available for hydration process might be less. Since the degree of hydration was known to be directly related to nonevaporable water of the paste, nonevaporable water determinations were made. The samples were taken after 8 hours of casting both from the open atmosphere and from the controlled 50 percent relative humidity

condition. The samples were vacuum oven dried for 36 hours and tests were run for nonevaporable water determination. It was found that the content of nonevaporable water in the paste was less when the experiment was run in an open condition than it was with the 50 percent controlled relative humidity (see Appendix Table 36 for nonevaporable water content).

One experiment was run passing laboratory air over the specimen directly. The laboratory relative humidity varied from 59 percent at the beginning of the experiment to 51 percent at the end of the experiment. The readings are tabulated in the Appendix Table 37. From this it was concluded that in an open condition more shrinkage occurred due solely to the greater evaporation rate. Consideration of carbonation shrinkage was eliminated when closed atmosphere tests showed no difference when the air had been passed through Mallcosorb, an indicating carbon dioxide absorbent. Since a small chamber was used to contain the experimental samples and the air was passed slowly through the chamber, entering and exiting at locations, about one inch above the sample, diffusion process was presumably taking place between the sample and flow of air. This was, of course, reflected by the increased shrinkages at lower humidities. One may recall that the humidity at the downstream end of the chamber was verified by humidity sensor and not found to differ from that expected from the acid bath system. However, it is believed that the open atmosphere resulted in air currents causing a greater rate of evaporation than occurred in the controlled condition. The discrepancy between open atmosphere and controlled

condition results did not invalidate the results insofar as comparing the different admixtures. It should be recognized, however, that natural exposures of cement paste to atmosphere will probably result in shrinkage greater than those reported for the same relative humidity in the controlled experiment.

The practical applications of this work are for concrete not for paste hence absolute shrinkage values are not relevant but the relative shrinkage i.e. those of different admixtures are relevant to concrete construction.

Plastic Shrinkage Cracking

In an effort to explain the mechanism of plastic shrinkage cracking, some facts concerning the initial hydration process need to be reviewed briefly.

Tricalcium silicate and tricalcium aluminate are considered to be the principal active components of portland cement at early stages of hydration. When tricalcium silicate reacts with water, calcium silicate hydrate is formed and lime is released into solution. On the other hand, tricalcium aluminate reacts with sulfate and calcium ions from the solution to form ettringite.

In a heat evolution curve of cement hydration, an initial rapid heat evolution occurs, when the cement and water brought into contact (18). The initial rapid hydration is followed by a dormant period which is due to the formation of a sulfoaluminate coating on the highly reactive tricalcium aluminate phase and initially formed calcium silicate hydrate gel on the tricalcium silicate phase.

A second peak, due to the continued hydration of the tricalcium aluminate and mainly due to additional hydration of tricalcium silicate, occurs at the end of dormant period, which is perhaps a couple of hours long. According to Verbeck (18), the initial setting time of cement paste lies after the end of the dormant period and before the point of maximum peak of the second heat generation. Powers(19), considered that the end of dormant period and the beginning of the second heat evolution peak, is due to break up of the coating of the hydration products that would allow an increase in the rate of hydration to take place. The breakup such as this coating, is attributed to the generation of an osmotic pressure caused by the difference of concentration between the bulk aqueous phase and anhydrous cement minerals. Indeed if the dormant period is caused by such a coating, at least a partial break up of the coating is necessary for an increase in the hydration. The heat evolution rate declines after the second peak; Powers (19) has discussed the details of the processes taking place here.

Lerch (4) reported that the plastic shrinkage cracks may develop when rate of evaporation exceeds the rate at which bleeding water rises to the surface causing the disappearance of the sheen from the surface. According to Ravina and Shalon (5), the appearance of the first plastic shrinkage crack consistently coincided with the transition from rapid shrinkage to the slow rate one. The reason given for this transition is the changes in the flow properties of the mortar, which in turn depend on the rate of hydration.

In the present work, it was observed that the appearance of plastic shrinkage cracks consistently coincided with the transition from rapid shrinkage to the slow rate one. This transition lies somewhere near the initial setting time of the cement paste. According to Verbeck (18), this initial setting time lies somewhere in between the end of dormant period and the maximum peak of the second heat of evolution. Up to the initial setting time, the sheen exists due to the low heat evolution in the dormant period which causes less rate of evaporation. As soon as dormant period is over the rate of heat evolution increases rapidly and evaporation is speeded up, and the disappearance of sheen from the surface occur. From the above discussion it should be noted that the disappearance of sheen from the surface is due to the increased rate of hydration and rate of evaporation.

Figures 15 and 16 show the specimens at 25 and 50 percent relative humidities. Comparing plain paste specimens in Figures 15 and 16, the number of cracks formed at 25 percent relative humidity is larger than the number of cracks formed at 50 percent relative humidity, as would be expected. This is true with all three retarding admixtures as well. The number of cracks formed in plain paste and pastes with retarding admixtures are more or less proportional to their plastic shrinkage. With hydroxycarboxylic acid retarder, the cracks are greater in number. Figure 17 (Appendix) shows the specimens at laboratory atmosphere. It can be seen that more cracks occurred due to greater shrinkage of the paste.

FIGURE 15 COMPARISON OF SPECIMENS AT 25% R.H.

1 Plain paste	2 Using lignosulfonate
3 Using carbohydrate	4 Using hydroxycarboxylic acid

FIGURE 16 COMPARISON OF SPECIMENS AT 50% R.H.

- 1 Plain paste
- 2 Using lignosulfonate
- 3 Using carbohydrate
- 4 Using hydroxycarboxylic acid

CONCLUSIONS

Based on the measurements of plastic shrinkage of specimens, the following conclusions seems to be reasonable. They apply only to the particular composition of cement used, condition and set up of the experiment.

1. Using retarding admixtures, plastic shrinkage is higher than the plastic shrinkage of plain paste. The higher shrinkage is due to the increased period of time spent in the plastic stage and, with some retarders, an increase in the amount of bleeding water.
2. The appearance of the first crack coincides with transition from a high initial rate of shrinkage to a slower rate. Since this transition approximately coincides with Vicat initial setting time, the rate of hydration and the rate of evaporation influence crack formation.
3. The rate of shrinkage varies for different admixtures when the relative humidity changes. This results in lignosulfonate giving the most uniform amount of shrinkage at different relative humidities.
4. The morphology of the plastic cement paste is apparently different for different admixtures are evidenced by difference in the bleeding and in rate of shrinkage.

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LIST OF REFERENCES

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APPENDIX

FIGURE 17 COMPARISON OF SPECIMENS AT LABORATORY CONDITION

1 Plain paste	2 Using lignosulfonate
3 Using carbohydrate	4 Using hydroxycarboxylic acid
	5 Using calcium chloride

FIGURE 18 -SHRINKAGE CURVES USING CALCIUM CHLORIDE .

FIGURE 19 - COMPARISON OF SHRINKAGE AT LABORATORY ATMOSPHERE.

TABLE 22 COMPARISON OF SHRINKAGES AT 25% R.H.

Water Cement Ratio: .35

Relative Humidity: 25.1

DATA

	Groups			
	1 Plain Paste	2 Lignosulfonate	3 Carbohydrate	4 Hydroxy Carboxylic Acid
Observations	3051	3644	4916	6187
	2967	3560	4746	5848
Total	6018	7204	9662	12035
Mean	3009	3602	4831	6017

 C_1 = Contrast: Plain Paste Vs Lignosulfonate C_2 = Contrast: Plain Paste Vs Carbohydrate C_3 = Contrast: Plain Paste Vs Hydroxy Carboxylic AcidANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among Groups	3	10737634.3	3579211.4	181.3
Contrast C_1	1	351669.0	351669.0	17.8
Contrast C_2	1	3319684.0	3319684.0	168.1
Contrast C_3	1	9051072.2	9051072.2	458.4
Within Groups	4	78966.5	19741.6	
Total Corrected	7	10816600.8		

$$F_{.01,3,4} = 16.7$$

$$F_{.01,1,4} = 21.2$$

TABLE 23 COMPARISON OF SHRINKAGES AT 50% R.H.

Water Cement Ratio: .35

Relative Humidity: 50%

DATA

	Groups			
	1 Plain Paste	2 Lignosulfonate	3 Carbohydrate	4 Hydroxy Carboxylic Acid
Observations	2542	3221	3644	4746
	2458	3136	3644	4831
Total	5000	6357	7288	9577
Mean	2500	3178.5	3644	4788.5

 C_1 = Contrast: Plain Paste Vs Lignosulfonate C_2 = Contrast: Plain Paste Vs Carbohydrate C_3 = Contrast: Plain Paste Vs Hydroxy Carboxylic AcidANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among Groups	3	5562500.5	1854166.8	689.7
Contrast C_1	1	460362.2	460362.2	171.2
Contrast C_2	1	1308736.0	1308736.0	486.8
Contrast C_3	1	5237232.2	5237232.2	1948.2
Within Groups	4	10753.0	2688.2	
Total Corrected	7	5573253.5		

 $F_{.01,3,4} = 16.7$ $F_{.01,3,4} = 21.2$

TABLE 24 - COMPARISON OF SHRINKAGES AT 75% R.H.

Water Cement Ratio: 0.35

Relative Humidity: 75%

DATA

	Groups			
	1 Plain Paste	2 Lignosulfonate	3 Carbo- hydrate	4 Hydroxy Carboxylic Acid
Observations	1356	2543	2204	3136
	1272	2458	2373	2967
Total	2628	5001	4577	6103
Mean	1314	2500.5	2288.5	3051.5

 C_1 = Contrast: Plain Paste Vs Lignosulfonate C_2 = Contrast: Plain Paste Vs Carbohydrate C_3 = Contrast: Plain Paste Vs Hydroxy Carboxylic acidANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among Groups	3	3153526.3	1051175.4	117.7
Contrast C_1	1	1407782.2	1407782.2	157.7
Contrast C_2	1	949650.2	949650.2	106.4
Contrast C_3	1	3018906.2	3018906.2	338.2
Within Groups	4		8925.3	
Total Corrected	7	3189227.8		

$$F_{.01,3,4} = 16.7$$

$$F_{.01,1,4} = 21.2$$

TABLE 25 SHRINKAGES FOR PLAIN PASTE

Water Cement Ratio: 0.35

DATA

	Groups		
	1. At 25% R.H.	2. At 50% R.H.	3. At 75% R.H.
Observations	3051	2542	1356
	2967	2458	1272
Total	6018	5000	2628
Mean	3009	2500	1314

 C_1 = Contrast: 25% R.H. Vs 50% R.H. C_2 = Contrast: 50% R.H. Vs 75% R.H.

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among groups	2	3025801.3	1512900.6	428.8
Contrast C_1	1	259081.0	259081.0	73.4
Contrast C_2	1	1406596.0	1406596.0	398.7
Within Groups	3	10584.0	3528.0	
Total	5	3036385.3		

$$F_{.01,2,3} = 30.8$$

$$F_{.01,1,3} = 34.1$$

TABLE 26 SHRINKAGES USING LIGNOSULFONATE

Water Cement Ratio: 0.35

DATA

	Groups		
	1. At 25% R.H.	2. At 50% R.H.	3. At 75% R.H.
Observations	3644	3221	2543
	3560	3136	2458
Total	7204	6357	5001
Mean	3602	3178.5	2500.5

 C_1 = Contrast: 25% R.H. Vs 50% R.H. C_2 = Contrast: 50% R.H. Vs 75% R.H.

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among groups	2	1234892.3	617446.1	172.2
Contrast C_1	1	179352.2	179352.2	50.0
Contrast C_2	1	459684.0	459684.0	128.2
Within Groups	3	10753.0	3584.3	
Total	4	1245645.3		

$$F_{.01,2,3} = 30.8$$

$$F_{.01,1,3} = 34.1$$

TABLE 27 SHRINKAGES USING CARBOHYDRATE

Water Cement Ratio: 0.35

DATA

	Groups		
	1. At 25% R.H.	2. At 50% R.H.	3. At 75% R.H.
Observations	4916	3644	2204
	4746	3644	2373
Total	9662	7288	4577
Mean	4831	3644	2288.5

 C_1 = Contrast: 25% R.H. Vs 50% R.H. C_2 = Contrast: 50% R.H. Vs 75% R.H.

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among groups	2	6473770.3	3236885.1	337.9
Contrast C_1	1	1408979.0	1408979.0	147.1
Contrast C_2	1	1837380.2	1837380.2	191.8
Within Groups	3	28730.5	9576.8	
Total	5	6502500.0		

$$F_{.01,2,3} = 30.8$$

$$F_{.01,1,3} = 34.1$$

TABLE 28 SHRINKAGES USING HYDROXYCARBOXYLIC ACID

Water Cement Ratio: 0.35

DATA

	Groups		
	1. At 25% R.H.	2. At 50% R.H.	3. At 75% R.H.
Observations	6187	4746	3136
	5848	4831	2967
Total	12035.0	9577	6103
Mean	6017.5	4788.5	3051.5

 C_1 = Contrast: 25% R.H. Vs 50% R.H. C_2 = Contrast: 50% R.H. Vs 75% R.H.

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among groups	2	8883177.3	4441588.6	176.8
Contrast C_1	1	1510441.0	1510441.0	60.1
Contrast C_2	1	3017169.0	3017169.0	120.1
Within Groups	3	75353.5	14117.8	
Total	5	8958530.8		

$$F_{.01,2,3} = 30.8$$

$$F_{.01,1,3} = 34.1$$

TABLE 29 COMPARISON OF SLOPES AT 25% R.H.

Water Cement Ratio: .35

Relative Humidity: 25%

DATA

	Groups			
	1 Plain Paste	2 Ligno- sulfonate	3 Carbo- hydrate	4 Hydroxy Carboxylic Acid
Observations	822.1	709.9	944.3	1021.6
	889.8	723.8	922.5	959.5
Total	1711.9	1433.7	1866.8	1981.1
Mean	855.9	716.8	933.4	990.5

 C_1 = Contrast: Plain Paste Vs Lignosulfonate C_2 = Contrast: Plain Paste Vs Carbohydrate C_3 = Contrast: Plain Paste Vs Hydroxy Carboxylic acid

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among Groups	3	84253.8	28084.6	24.67
Contrast C_1	1	19336.7	19336.7	16.9
Contrast C_2	1	6002.9	6002.9	5.27
Contrast C_3	1	18120.8	18120.8	15.9
Within Groups	4	4553.0	1138.2	
Total Corrected	7	88806.8		

 $F_{.01,3,4} = 16.7$ $F_{.01,1,4} = 21.2$

TABLE 30 COMPARISON OF SLOPES AT 50% R.H.

Water Cement Ratio: 0.35

Relative Humidity: 50%

DATA

	Groups			
	1 Plain Paste	2 Ligno- sulfonate	3 Carbo- hydrate	4 Hydroxy Carboxylic Acid
Observations	711.1	547.1	468.6	725.7
	745.7	527.3	490.9	750.6
Total	1456.8	1074.5	959.5	1476.3
Mean	728.4	537.2	479.7	738.1

 C_1 = Contrast: Plain Paste Vs Lignosulfonate C_2 = Contrast: Plain Paste Vs Carbohydrate C_3 = Contrast: Plain Paste Vs Hydroxy Carboxylic acidANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among Groups	3	104428.2	34809.4	103.0
Contrast C_1	1	36535.6	36535.6	108.1
Contrast C_2	1	61804.3	61804.3	182.9
Contrast C_3	1	95.3	95.3	0.28
Within Groups	4	1351.1	337.7	
Total Corrected	7	105779.4		

$$F_{.01,3,4} = 16.7$$

$$F_{.01,1,4} = 21.2$$

TABLE 31 COMPARISON OF SLOPES AT 75% R.H.

Water Cement Ratio: 0.35

Relative Humidity: 75%

DATA

	Groups			
	1 Plain Paste	2 Ligno- sulfonate	3 Carbo- hydrate	4 Hydroxy Carboxylic Acid
Observations	339.1	429.1	303.5	400.3
	318.4	467.8	315.9	361.1
Total	657.5	896.9	619.4	761.4
Mean	328.7	448.4	309.7	380.7

 C_1 = Contrast: Plain Paste Vs Lignosulfonate C_2 = Contrast: Plain Paste Vs Carbohydrate C_3 = Contrast: Plain Paste Vs Hydroxy Carboxylic acidANALYSIS OF VARIANCE TABLE

Source		Sum of Squares	Mean Squares	F-Ratio
Among Groups	3	2313.4	7710.4	17.1
Contrast C_1	1	14321.1	14321.1	31.7
Contrast C_2	1	363.8	363.8	0.8
Contrast C_3	1	2696.6	2696.6	5.9
Within Groups	4	1804.9	451.2	
Total Corrected	7	24936.3		

$$F_{.01,3,4} = 16.7$$

$$F_{.01,1,4} = 21.2$$

TABLE 32 SLOPES FOR PLAIN PASTE

Water Cement Ratio: .35

DATA

	Groups		
	1. At 25% R.H.	2. At 50% R.H.	3. At 75% R.H.
Observations	822.1	711.1	339.1
	889.8	745.7	318.4
Total	1711.9	1456.8	657.6
Mean	855.9	728.4	328.8

 C_1 = Contrast: 25% R.H. Vs 50% R.H. C_2 = Contrast: 50% R.H. Vs 75% R.H.

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among groups	2	302564.4	151282.2	146.2
Contrast C_1	1	16269.0	16269.0	15.7
Contrast C_2	1	160830.3	160830.3	155.4
Within Groups	3	3104.2	1034.7	
Total	5	305668.7		

 $F_{.01,2,3} = 30.8$ $F_{.01,1,3} = 34.1$

TABLE 33 SLOPES USING LIGNOSULFONATE

Water Cement Ratio: 0.35

DATA

	Groups		
	1. At 25% R.H.	2. At 50% R.H.	3. At 75% R.H.
Observations	709.9	527.4	429.2
	723.8	547.1	467.8
Total	1433.8	1074.5	896.9
Mean	716.9	537.2	448.4

 C_1 = Contrast: 25% R.H. Vs 50% R.H. C_2 = Contrast: 50% R.H. Vs 75% R.H.

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among Groups	2	74804.3	37402.2	108.4
Contrast C_1	1	32268.3	32268.3	93.5
Contrast C_2	1	7884.4	7884.4	22.8
Within Groups	3	1034.9	344.9	
Total	5	75839.3		

 $F_{.01,2,3} = 30.8$ $F_{.01,1,3} = 34.1$

TABLE 34 SLOPES USING CARBOHYDRATE

Water Cement Ratio: 0.35

DATA

	Groups		
	1. At 25% R.H.	2. At 50% R.H.	3. At 75% R.H.
Observations	944.3	468.6	303.5
	922.5	490.9	315.9
Total	1866.8	959.6	619.4
Mean	933.4	479.8	309.7

 C_1 = Contrast: 25% R.H. Vs 50% R.H. C_2 = Contrast: 50% R.H. Vs 75% R.H.

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among Groups	2	415815.9	207907.9	1109.4
Contrast C_1	1	205783.3	205783.3	1098.4
Contrast C_2	1	28926.1	28926.1	154.4
Within Groups	3	562.2	187.4	
Total	5	416378.1		

 $F_{.01,2,3} = 30.8$ $F_{.01,1,3} = 34.1$

TABLE 35 SLOPES USING HYDROXYCARBOXYLIC ACID

Water Cement Ratio 0.35

DATA

	Groups		
	1. At 25% R.H.	2. At 50% R.H.	3. At 75% R.H.
Observations	1021.6	725.7	400.3
	959.5	750.6	361.1
Total	1981.1	1476.3	761.4
Mean	990.6	738.2	380.7

 C_1 = Contrast: 25% R.H. Vs 50% R.H. C_2 = Contrast: 50% R.H. Vs 75% R.H.

ANALYSIS OF VARIANCE TABLE

Source	Deg. of Freedom	Sum of Squares	Mean Squares	F-Ratio
Among Groups	2	375583.1	187791.5	187.3
Contrast C_1	1	63703.9	63703.9	63.5
Contrast C_2	1	127765.8	127765.8	127.4
Within Groups	3	3007.5	1002.5	
Total	5	378590.6		

 $F_{.01,2,3} = 30.8$ $F_{.01,1,3} = 34.1$

TABLE 36 NON-EVAPORABLE WATER DETERMINATION

Container Nos.	1	2	3	4
Weight of sample	0.4776	0.4914	0.3530	0.3701
Weight of non-evaporable water (W_n)	0.0255	0.0244	0.0246	0.0249
Weight of dry sample	0.4521	0.4670	0.3286	0.3452
W_n /wt. of dry sample	0.0560	0.052	0.0740	0.0720

Note:

- 1) Weights in g.
- 2) Container Nos. 1 and 2 contains sample from specimen kept in laboratory condition.
- 3) Container Nos. 3 and 4 contains sample from specimen kept in controlled 50 percent relative humidity.
- 4) Samples are vacuum oven dried for about 36 hours.
- 5) Non-evaporable water from PEN FIELD TEST.

TABLE 37 SHRINKAGE OF PLAIN PASTE BY PASSING LABORATORY AIR
DIRECTLY OVER THE SPECIMEN

Relative humidity varied from 59% when experiment started to 51%
at the end of the experiment. Temperature is about 24°C

Time (hours)	Voltmeter Reading (volts)	Change in Probe Gap (inches)	Linear Shrinkage (millionths)
0	2.260	--	--
1	2.310	0.0010	170
2	2.470	0.0030	509
3	2.740	0.0075	1272
4	3.100	0.0120	2034
6	3.240	0.0140	2373

SAMPLE OF CALCULATION:

Change in probe gap at one hour = (probe gap, at one hour -
probe gap at zero hour) from calibration curve.

i.e. change in probe gap at one hour = 0.0510 - 0.0500
= 0.001 inch

$$\begin{aligned}
 \text{Linear shrinkage in millionths} &= \frac{\text{Change in probe gap}}{5.9 \times 10^6} \\
 &= \frac{0.001}{5.9 \times 10^6} \\
 &= 170
 \end{aligned}$$