SCHOOL OF CIVIL ENGINEERING

JOINT HIGHWAY RESEARCH PROJECT

JHRP-77-10

STUDIES ON CEMENT PASTE AND CONCRETE BOTH MADE WITH LOW POROSITY CEMENT

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PURDUE UNIVERSITY
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STUDIES ON CEMENT PASTE AND CONCRETE
BOTH MADE WITH LOW POROSITY CEMENT

TO: J. F. McLaughlin, Director
Joint Highway Research Project

July 6, 1977

File: 5-14-7

FROM: H. L. Michael, Associate Director
Joint Highway Research Project

Project: C-36-61G

Attached is a Final Report on the JHRP Research Study titled "Ultra High Strength, Low Porosity Concrete". The Report is titled "Studies on Cement Paste and Concrete Both Made with Low Porosity Cement". The Study has been conducted by Mr. Carlos Gomez-Toledo, a graduate researcher studying in the School of Civil Engineering while on leave from the Consejo Nacional de Ciencia y Tecnologia of Mexico. Professor Sidney Diamond directed the Study.

The Report is presented as fulfillment of the objectives of the Study as approved in December 1975.

Respectfully submitted,

Harold L. Michael

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Associate Director

HLM/ss

Attachment

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Final Report

STUDIES ON CEMENT PASTE AND CONCRETE BOTH MADE WITH LOW POROSITY CEMENT

by

Carlos Gomez-Toledo

Graduate Fellow

Joint Highway Research Project

Project No.: C-36-61G

File No.: 5-14-7

Prepared as Part of an Investigation

Conducted by

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in cooperation with the

Indiana State Highway Commission

Purdue University
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Finally, the writer expresses his deepest appreciation to his mother and brothers from whom he received enormous support and continuous encouragement.

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ABSTRACT

Gómez-Toledo, Carlos. M. S. C. E., Purdue University, May 1977, Studies on Cement Paste and Concrete both Made With Low Porosity Cement. Major Professor: Sidney Diamond.

Cement paste and concrete, both made with "low porosity" cement - finely ground gypsum-free clinker regulated with an admixture of a specially formulated sulfonated lignin and sodium bicarbonate - were examined in detail. The W:C ratio levels explored in the cement paste were 0.22, 0.23 and 0.24, and in the concrete 0.26, 0.28, 0.30 and 0.32. Studies were carried out to determine the influence of variations in the admixture content and of the cement content on the workability and on the compressive strength of concrete. Most of the concretes investigated had a cement factor of 8.0 bags per cu yd (450 Kg/m^3), an aggregate-to-cement ratio of about 4.2, and a coarse-to-fine aggregate volume ratio of 1.0.

On cement paste, studies were carried out on the rheological behavior prior to hardening, on the hydration process, on the microstructure of the hardened products, on compressive strength, on permeability and on pore size distribution. For concrete, the properties investigated included rheological behavior and workability in the fresh state and compressive strength, flexural strength, and dynamic modulus of elasticity in the hardened condition.

It was found that excellent consistency and flow behavior could be produced in both cement pastes and concrete formulated at low water contents. Concrete made at W:C 0.30, for instance, was free-flowing without vibration, was "self-compacting," and showed no sign of segregation.

In trials in which the admixture concentrations were varied it was found that sulfonated lignin contents of 0.66% or greater by weight of cement produced satisfactory mixes with respect to workability and the compressive strengths of the concretes were not affected by variations in the lignin content. It was found that $NaHCO_3$ contents of 0.8% and 1.0% yielded workable concretes, but at 1.4% and higher the workability of the concrete was somewhat impaired. The development of compressive strength of concrete was not affected by $NaHCO_3$ contents varying between 1.0 and 1.6%; but reducing the content to 0.8% resulted in a significant delay in strength gain. This effect was found to be temporary; from 7 days on, the compressive strength of the concrete was found to be entirely independent of its $NaHCO_3$ content.

Satisfactory low porosity concrete was produced at a cement content of 8.0 bags per cu yd (450 Kg/m^3). Lower cement contents produce a loss of consistency and a degradation of the flow properties of the fresh concrete. Higher cement contents, on the other hand, markedly improved the workability of concrete and increased its compressive strength, but the latter only marginally.

Low porosity concretes exhibited a short useful working time of about 30 to 60 minutes. Longer working times were observed for higher W:C ratios and for higher sulfonated lignin content-to-$NaHCO_3$ content ratios.

It was found that hydration of the paste was small over the first 18 hours or so, but then accelerated markedly, the degree of hydration at two days being 80% of the corresponding parameter at 90 days. The microstructure developed by the paste was found to be somewhat different from that of conventional Portland cement paste. Little or no AFt product was formed. At two days a massive matrix of "fused" hydration products composed basically of C-S-H gel and $Ca(OH)_2$ was found to exist, and this microstructure was not significantly altered even at 90 days.

The time of setting of low porosity cement paste was found to coincide accurately with the end of its dormant period as indicated by temperature evolution measurements. Delay in the set time and in the hydration stage corresponding to onset of rapid reaction in the paste seemed to be associated with relative humidities in the laboratory air higher than 75% RH.

For concrete, compressive strength development was rapid following the first day, concrete strengths of about 39 MPa (5,700 psi) developing at 2 days, 53 MPa (7,700 psi) at 3 days, and 70 MPa (10,000 psi) at 28 days, with room temperature curing.

Besides the relatively high compressive strength levels rapidly developed by low porosity concrete, it was also observed that flexural strengths and dynamic elastic modulii were significantly higher than would be expected for high-strength concretes of similar compressive strength made with ordinary Portland cement.

Permeability measurements and pore size distribution determinations suggested that low porosity cement paste is much less permeable, less porous, and "tighter" than ordinary Portland cement paste at any given age.

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Concrete Properties as Related to Porosity and Water:Cement Ratio

Strength and dimensional stability are highly desired properties in concrete. While many factors influence these properties, porosity has been considered to be the dominant contributor. While the behavior of concrete is more complex than that of cement paste due to the contribution of the aggregate and of paste-aggregate interaction, strength and shrinkage of concrete are generally considered to reflect the corresponding parameters of the cement paste present within the concrete to some considerable extent. Powers (20) found that the gel-space ratio x is related to the compressive strength, f_c, of cement paste by the equation

$$f_c = f_c^\circ x^n \quad ,$$

where f_c° and n are empirical constants. The higher the porosity of the paste the lower the value of x and, consequently, the less the compressive strength of the paste. Beaudoin and MacInnis (2) concluded that the volume concentration of hydrate substance, and hence the porosity, appears to be the most important strength parameter of portland cement paste regardless of the presence of admixtures. More recently, Roy and Gouda (22) and Feldman and Beaudoin (9) also found porosity to be a major factor influencing the strength of cement paste.

Thus, superior concrete should be designed in such a way that porosity of its cement paste component should be at a reasonable minimum as limited by the rheological requirement for proper placing of the concrete. Porosity values in concrete may be significantly decreased by either using vacuum processing techinques (10), or lowering the water to cement ratio (W:C ratio) of its constituent paste.

Experimental evidence shows that in both cement pastes and concretes, a reduction of the water content (other factors being kept unchanged) is accompanied by change in rheological behavior in the direction of increased stiffness. This change is due to the increased frictional resistance between the layers of the concrete, the increase in viscosity in the cement paste, and the decrease in separation among the individual particles in the concrete. This effect is noticeable in conventional concrete mixes whose W:C ratios approach 0.40; "dry," "very dry," and "no-slump" are some common adjectives used to designate this kind of concrete. The increase of stiffness of such concretes has been sucessfully overcome through the use of additives or admixtures and even some decrease in the water demand of the mix to meet specific workability requirements has been achieved.

The present use of water-reducers in cement and concrete technology is widespread. The amount of reduction in the original water content of the paste one can get and still get placeable concrete by the conventional use of these chemicals is about 10 percent. Strong water reducing compounds, capable of usefully reducing the water requirement of cement paste and concrete up to about 30 percent, were commercially used in Japan as early as the late 1970's and in Germany and England by 1972 (1, 12). These are known as "superplasticizers" or "super water-reducers." Concrete made with them and designed to be free-flowing is called "flowing concrete," "superplasticized concrete," and "fluid concrete." Further comments on superplasticizers and their effect in cement paste and concrete will be made in Chapter IV.

Effects of Cement Fineness

Cement fineness is another parameter that influences porosity of cement paste and, to some extent, its compressive strength. The higher the cement fineness, the higher the strength of the paste, as shown by Price (21) and Czernin (7). Increasing cement fineness carries with it additional effects (16, 13) such as producing less stiff mixes, more rapid development of strength, slightly higher water demand, increase in the gypsum requirement for proper retardation, and decrease of bleeding. These effects will be discussed in Chapter IV.

Low-Porosity Cements

The Portland cement referred to previously is Portland cement clinker interground with gypsum as an agent to control its setting and the dimensional stability of the paste made with it. Luk'yanova, Segalova, and Rehbinder (15), using ground clinker without gypsum, carried out an investigation to study the effect of a hydrophilic plasticizer additive (calcium lignosulfonate) on the properties of cement pastes. They made cement pastes having as low a W:C ratio as 0.25. Furthermore, they compared the compressive strength vs. time (0-4 hours) curves of cement pastes having W:C 0.25 and W:C 0.40 and found that the W:C 0.25 cement pastes were roughtly seven times stronger than thoses having W:C 0.40. Flash setting of these cement pastes (without gypsum) did not take place due to the retardant effect of the adsorbed lignosulfonate.

Cements can be specially formulated from ground clinker and various set retarding agents (other than gypsum). A class of these, formulated with a combination of an alkali carbonate or bicarbonate and a lignosulfonate especially for the purposes of providing workability at low water contents has been designated as "low porosity" cements.

Stephen Brunauer and coworkers, at Clarkson College of Technology, New York, carried out a thorough investigation on a number of low porosity cement pastes. A complete report of this work was published in 1972-73 (4, 5, 17, 18, 28, 29, 30). The admixtures used in their work were calcium lignosulfonate and potassium carbonate. They observed that the use of clinker ground to approximately normal fineness, 4,000 to 4,300 cm^2/g Blaine, gave results that were unsatisfactory due to slow initial hydration, and to low ultimate strength. Subsequently they carried out work on finely ground clinkers; a Type I and a Type II clinkers, each ground to a fineness of 6,000 to 9,000 cm^2/g (Blaine) with the aid of a variety of grinding aids.

Yudenfreund and co-workers (30) were able to make cement pastes of excellent workability and satisfactory setting times with as low W:C ratio as 0.20, by weight. In their studies, they investigated consistency in the fresh state, compressive strength, dimensional stability, non-evaporable water content, degree of hydration, density, and pore structure of hardened cement paste.

One of the impressive results obtained in this investigation was the compressive strength of the cement paste; values of 100 MPa (15,000 psi) at one day and 200 MPa (30,000 psi) at 90-day hydration times being recorded (28).

Experiments on concrete made with low porosity cement subsequently carried out in the American Cement Technical Center, Riverside, Calif., were reported by Skalny, Phillips and Cahn (23). These authors worked with Type II cement clinkers ground to different fineness ranging from 5,200 to 8,000 cm^2/g (Blaine), and regulated with calcium lignosulfonate and potassium carbonate. They made concrete mixes having W:C ratios ranging from 0.35 down to 0.26 with most of the work reported being on 0.26 W:C ratio concrete. Preliminary trials with these concretes indicated that strength developed only slowly with room temperature curing, and that steam curing was required to obtain high strength.

Skalny et al. reported measurements on the rheology of the fresh concrete so produced, and on compressive and flexural strength, shrinkage, and freezing and thawing response of concretes after steam curing and subsequent hydration at room temperature. It appeared that mixes on the wet side, ca. 0.35 W:C ratio, showed good workability characteristics as indicated by the Vebe times recorded, but that concretes mixed at W:C less than 0.30 showed relatively poor workability, as indicated by Vebe times as long as 3 minutes. However, as expected, the compressive strengths of the lower W:C mixes were significantly higher than those mixed at higher water contents. For the lower W:C ratio mixes, compressive strengths were of the order of 69 MPa (10,000 psi) for specimens that were steam cured and hydrated for one day additionally, and up to 97 MPa (14,000 psi) for specimens hydrated for 28 days after steam curing.

Properties of Low-Porosity Cements and Concrete Investigated in the Present Work

The present work deals with the study of some properties of cement paste and of concrete both made with a low porosity cement (without gypsum) formulated from an ordinary clinker of composition equivalent to that of a Type I cement. The admixtures used throughout the investigation were a specially formulated sulfonated lignin (sodium form), and sodium bicarbonate, $NaHCO_3$. Patents for the manufacture of such low porosity cements (25, 26) were claimed by Westvaco Corporation, New York, N. Y., in 1976.

For cement paste, the properties investigated were the flow behavior of the fresh pastes, and the temperature evolution. For hardened cement pastes they included the composition and microstructure (by x-ray diffraction, DTA, and SEM), the compressive strength, the degree of hydration, the pore size distribution, and the permeability. For concrete, the properties investigated included rheology and air content of the fresh concrete, and compressive strength and dynamic modulus of elasticity of hardened concrete, as functions of age. Concretes made in this investigation set normally in approximately one and one-half hours and steam curing was not required for strength gain.

In the next chapters, details on the material used and on the experimental work followed in the investigation will be given. The results obtained will be presented and discussed, and finally some conclusions will be pointed out.

CHAPTER II

MATERIALS

The following is a description of the materials used in the present work.

Cement

The cement used was a standard Type I clinker made during a normal production run at the Holly Hill, South Carolina plant of the Giant Cement Company, in December 1974. Since the testing reported here was carried out in 1976 and the early part of 1977, the results obtained may reflect some deterioration due to aging.

The clinker was ground in a specially cleaned grinding mill free of all contact with gypsum to a measured Blaine fineness of 5,400 cm^2/g. A typical chemical analysis of clinker supplied by this plant during the period of manufacture is given in Table 1.

Admixtures

The sulfonated lignin used in the set-regulating admixture is a material produced in experimental quantities by the Westvaco Corporation, North Charleston, South Carolina, and designated by them "REAX LP." The material is prepared from purified Kraft-process pine lignin and is

Table 1. Plant Analysis of Typical Clinker.*

	percent
SiO_2	22.17
CaO	67.57
Al_2O_3	6.18
Fe_2O_3	2.63
MgO	1.06
SO_3	0.13
Na_2O	0.07
K_2O	0.17
Loss on Ignition	0.35
Soluble K_2O	0.04
Soluble Na_2O	0.01
Free CaO	0.69

Bogue Calculated Composition	
C_3S	58.2%
C_2S	19.7%
C_3A	11.9%
C_4AF	8.0%

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* Supplied by the Giant Cement Company Inc.

completely free of all sugars and other carbohydrates. It has been subjected to a controlled sulfonation process subsequent to its recovery, and is supplied as the sodium salt.

Sand

The fine aggregate used came from a local supplier and is composed of clean siliceous sand of the gradation given in Table 2. The fineness modulus was 2.85. Additional determinations on the properties of the fine aggregate included: dry rodded unit weight, 1,765 Kg/m^3 (110 lb/ft^3), in accordance with ASTM Designation:C 29-71, bulk specific gravity (SSD), 2.51, and absorption, 2.27%, both determined in accordance with ASTM Designation:C 128-68. The sand was oven dried prior to batching the concrete mixes.

Coarse Aggregate

The coarse aggregate used for most of this work was a hard, clean dolomite crushed rock from a quarry located at Delphi, Indiana. In addition, considerable preliminary work was done with a local river gravel. The gradation of the crushed rock meets the requirements ASTM Designation:C 33-71a for nominal size 67. Additional properties determined for the coarse aggregate included: dry rodded unit weight, 1,665 Kg/m^3 (104 lb/ft^3), determined in accordance with ASTM Designation:C 29-71, bulk specific

Table 2. Sieve Analysis of Fine Aggregate.

Sieve Number (mm)	Cumulative Percentage Retained
4 (4.75)	0.2
8 (2.36)	12.3
16 (1.18)	32.4
30 (0.60)	55.1
50 (0.30)	87.7
100 (0.15)	97.7

gravity (SSD), 2.74, and absorption, 0.67%, both determined as indicated in ASTM Designation:C 127-73. All the aggregate was oven dried before use.

CHAPTER III

EXPERIMENTAL METHODS

General details concerning the procedures followed to investigate properties of cement paste and concrete with low porosity cement will be described in this chapter, along with details of the equipment used, techniques for obtaining samples, and other pertinent information.

First, the sequence followed in making the cement pastes will be described and then the methods used for each investigation of the properties inferred will be detailed. The same order of description will be kept for concrete as well.

Methods Used With Cement Paste

All the cement pastes of the present work were made with the low porosity cement previously described, the special sulfonated lignin, $NaHCO_3$, and deionized water. Three different water to cement weight ratios were investigated: 0.22, 0.23 and 0.24. All cement paste batches were made with 1,000 g of cement.

The sulfonated lignin content was kept at 0.84% of the weight of the cement, and the sodium bicarbonate at 1.44%.

In mixing the pastes the sodium bicarbonate was first dissolved in the mix water (by stirring for about 30 seconds); then the sulfonated lignin was added with intermittent stirring until completely dissolved. The previously weighed batch of ground clinker was then added to this solution, using a procedure modified slightly from that described in ASTM Designation:C 305-70 to accomplish the mixing in a reproducible manner.

Details of Mixing

A standard Hobart mixer, Type N-50, capacity 4.73 dm^3, was used in mixing the pastes. The mix water containing the dissolved sodium bicarbonate and sulfated lignin was first poured into the mixer bowl. The ground clinker was then poured into the bowl and spread to cover all the solution. A 30 second period, beginning from the moment the clinker was put in contact with the solution, was allowed for absorption. This was followed by an initial mixing period of 45 seconds at the low-speed setting, and a waiting period of 90 seconds. During the first 30 seconds of this waiting period the paste was scraped down from the sides of the bowl, and the mix was covered with a wet towel to minimize evaporation.

The 90 second waiting period was followed by a second mixing period, the second mixing being done at the medium speed setting. The length of this period varied with the W:C ratio, being 60 seconds for the

W:C 0.24 pastes, 105 seconds for the W:C 0.23 pastes, and 150 seconds for the W:C 0.22 pastes. Additional vibration was found necessary for the W:C 0.22 pastes, accomplished by placing the bowl on a Syntron vibrating table set at 100 vibrations per second, and holding it firmly for 10 seconds.

After mixing was over, the W:C 0.24 and 0.23 pastes were visually uniform, and easy to pour; but invariably, the W:C 0.22 pastes had a small percentage - perhaps 1% - of unwetted cement grains, and were a little difficult to pour, with partial tearing or separation of the paste being poured taking place. One caution needed to be observed: the shearing resistance of the paste being mixed changes drastically with time, and a point is reached in the mixing cycle where it is too high for the capacity of the mixer used; it is necessary then to firmly hold the bowl to the bowl support ring to make the mixer function properly. This was done in all cases.

The mixing procedure just described differs from that given the standard (ASTM Designation:C 305-65) in the waiting period after the first mixing; the standard suggests a 15 second period and in this work a 45 second waiting period was found to be more effective with regard to water uptake. Furthermore, the standard suggests that the last mixing period should be one minute for all pastes. This period was found to be inadequate for the low porosity cement pastes having W:C 0.22 and W:C 0.23, these pastes yielding stiff, non-uniform pastes when mixed for only one minute.

One peculiarity observed in these studies was a relationship between the appearance of the paste after a specific degree of mixing and the ambient RH of the laboratory air. If mixing was carried out at room temperature (about 24°C) but at RH levels of about 32% RH or less, it was found that the mixing schedule described above would not be satisfactory. In the last stages of mixing at normal RH values, about 10 seconds before the end of the mixing schedule for W:C 0.23 pastes and about 25 seconds before the end of the mixing schedule for the W:C 0.24 pastes, the character of the cement-water mixture changes suddenly. It changes from an apparently stiff mixture that subdivides into several portions each of which rotates independently and follows the motion of the paddle around the bowl, to a flowing suspension that the paddle shears through readily and mixes uniformly. If the RH is less than 32%, the conversion to the last stage fluid mix is delayed and the mixing schedule described does not produce satisfactory results.

Consistency

The consistency of the low porosity cement pastes was qualitatively observed and attempts were made to study its viscometric behavior using the Brookfield Rheometer manufactured by Brookfield Engineering Laboratories, Inc., Stoughton, Ma. These were largely unsuccessful at the low W:C ratios employed.

Setting Time

The basic method described in ASTM Designation:C 191-71 was followed to determine the time of setting of the cement paste. Alternations in the procedure with respect to the mold, the way the paste should be cast, and the details of the determination were found to be necessary.

The fluidity of the pastes caused some leakage and sliding problems of the mold in early determinations of the setting time. These problems were solved by providing a rigid base plate for the mold and a suitable clamping device between the mold and the base plate (see Figure 1).

The cement paste was poured into the mold in one single layer, the top surface of which was about 2.0 mm below the height of the mold. After casting, the mold and its contents were wrapped with plastic and a wet towel placed over it. This arrangement was left undisturbed in the laboratory while not under testing.

Because of the unusual suddenness of setting of these pastes (once setting began) it was necessary to change the standard Vicat needle penetration from the 25.0 mm designated by ASTM C 191-71, for the initial setting time, to a needle penetration of 3.0 mm or less. As the setting of the paste (initial set and final set) takes place

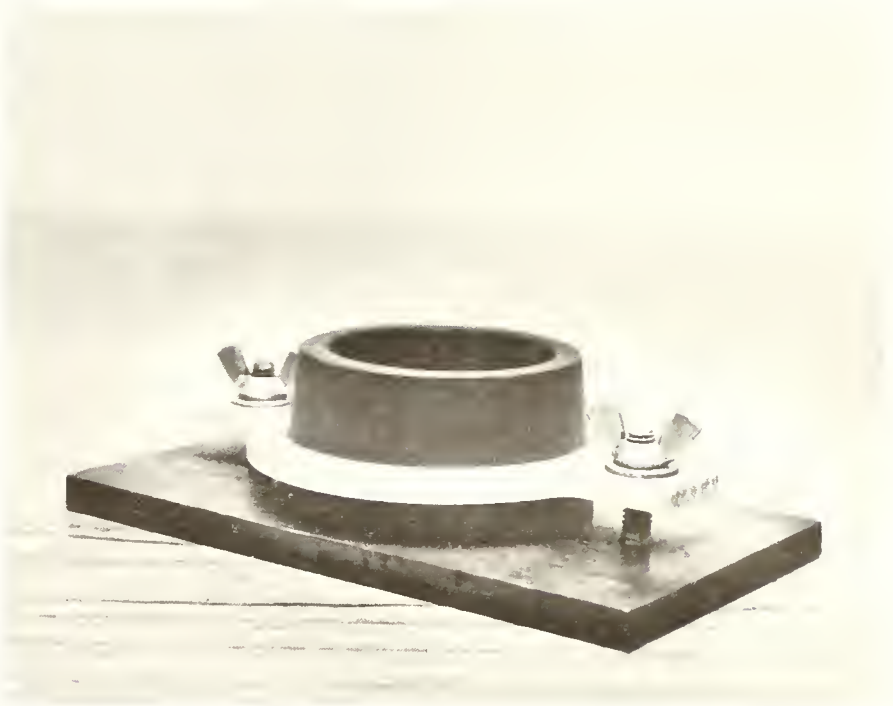

Figure 1. Vicat Apparatus Setting Time Mold.

suddenly in low porosity cement pastes, it was simply not possible to isolate a stage in the setting record approaching the 25.0 mm penetration.

Temperature Evolution

A device developed by Professor D. N. Winslow was used to measure the temperature evolution of low porosity cement paste during hydration. The general arrangement consisted of a styrofoam insulating system, two plastic containers (one for the paste under study, and one for the reference material), a set of two thermistors, a wheatstone bridge, and a recorder (see Figure 2).

Cement paste, made as described on page 15 was cast in one single layer in one of the plastic containers. The reference material used in this work was Ottawa sand (20-30 mesh) mixed with water, having a water:sand ratio equal to the W:C ratio of the paste under test. This reference material was put in the other plastic container. Immediately after casting the paste the container was sealed and the styrofoam lid fitted to isolate the system. The thermistors were then immersed in copper tubes that had one end crimped shut and that were embedded, one in the reference material, and the other in the cement paste; mercury had been previously poured into the copper tubes to provide adequate thermal conductivity between the inside copper tube wall and the thermistor to be inserted in the tube later on. The exothermic reaction of the

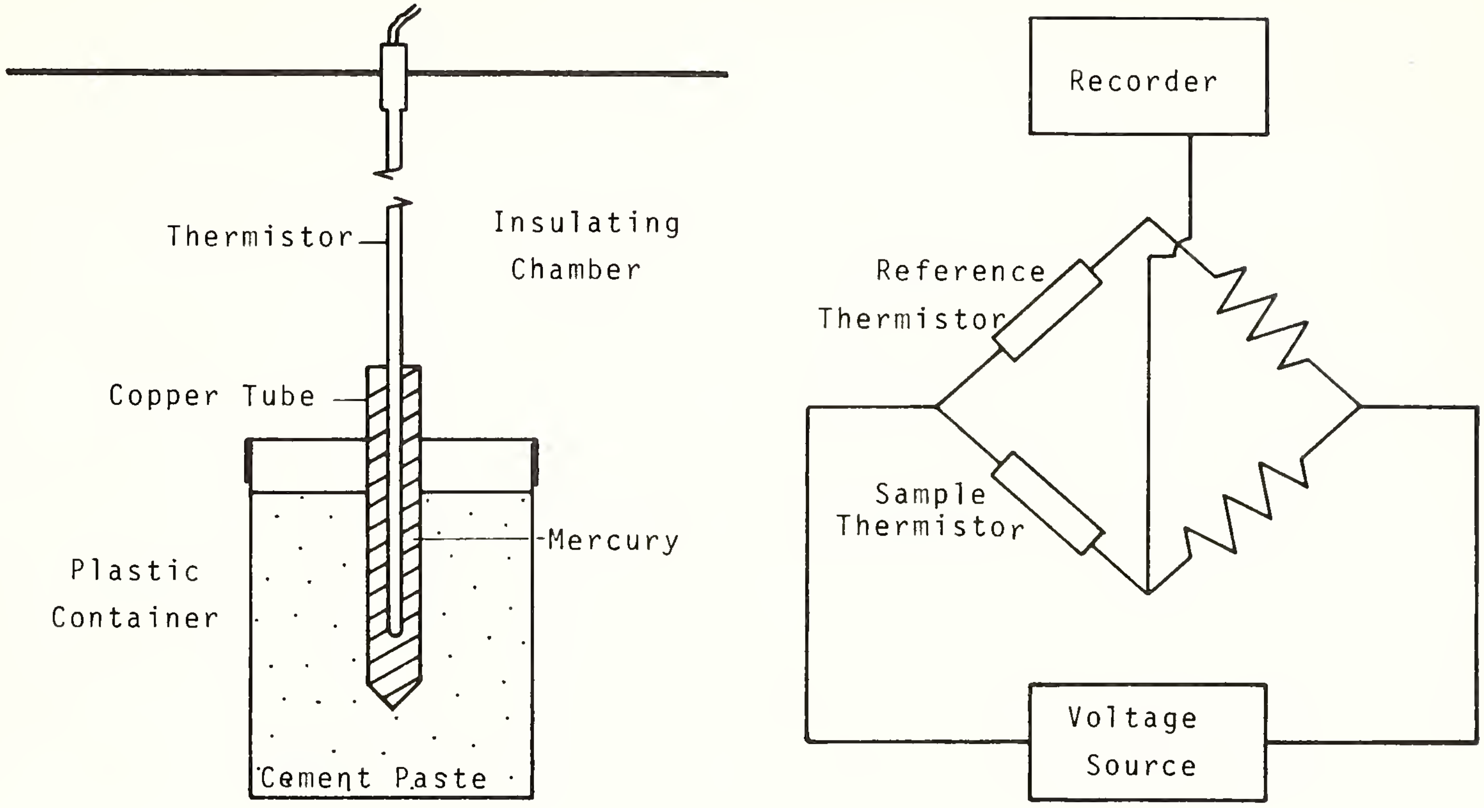

Figure 2. Temperature Evolution Device.

paste hydration processes raises the temperature of the thermistor embedded in tube in contact with the paste, causing a voltage difference between the two branches of the wheatstone bridge circuit to which the thermistors are connected. This voltage difference is fed into a recorder. Before the test is run the voltage differences corresponding to specified temperature differences are calibrated using water at different temperatures on the "test" side of the system.

X-Ray Diffraction

All the samples analyzed were taken from tested (broken) cube specimens. Care was taken to avoid the collection of pieces coming from the contact area between the specimen and the mold itself. Immediately after being collected, the samples were further crushed using a metallic crusher and screened through the No. 8 (2.36 mm) sieve. The portion of the material passing the No. 8 sieve was then immediately placed in a glass container and flooded with acetone to stop the hydration process. One minute later the excess acetone was poured out of the container and the sample placed in the oven at 105°C for overnight drying. The dry samples were pulverized using a SPEX mechanical shaker, and screened through a No. 100 (150 mm) sieve. Random powder mounts were prepared for X-ray diffraction.

A Siemens X-ray Diffractometer, Type F, equipped with ORTEC detector system was used for the x-ray work, carried out with CuK_{α} radiation. The diffractometer angle range covered was from 10° to 60°, 2Θ. The x-ray runs were performed under the following conditions: voltage, 40 kV; amperage, 28 ma; beam slit, 1/4°; time constant, 3 seconds; goniometer speed, 2°/minute.

Differential Thermal Analysis

Samples of cement paste pieces taken from tested (broken) cube specimens were further ground and screened through a No. 8 (2.36 mm) sieve. Hydration was stopped and the sample was dried in the oven, at 105°C, overnight. The dry samples were crushed with a porcelain mortar and screened through a No. 200 (75 μm) sieve.

A D-6000 Deltatherm III DTA apparatus, (manufactured by Technical Equipment Corporation, Denver, Co.), was used along with a Sargent SRG recorder. The parameters used throughout the DTA work were: heating rate, 10°C/min; differential temperature sensitivity, 1 in./°C; upper heating limit, 1,000°C. Fired kaolinite was used as the reference material.

Scanning Electron Microscopy

An air-free cement paste, W:C ratio 0.22, was especially made to obtain samples for SEM analysis. The mixing was achieved by introducing the materials in an evacuated chamber and agitating it with a paint shaker mechanical vibrator for 5 minutes. At the end of this period the chamber was opened and vibrated for 20 seconds on a Vebe vibrating table. The paste was poured into vials, demolded a day later, and immersed in water for curing. At the desired age the paste was crushed, hydration was stopped by acetone treatment, and the material vacuum-oven dried.

Additional specimens from fractured (tested) cement paste cubes prepared as previously described were also examined.

Dried specimens were fractured and mounted on aluminum stubs for SEM examination, the fresh fracture surfaces facing upward. Electrical conductivity between the specimen and the stub was achieved by mixing silver dag with the Duco cement used to mount the specimens. The specimens were then coated to a nominal coating thickness of 200 Å of a gold-palladium alloy using a sputter-type coater (Hummer I model manufactured by Technics, Inc., Alexandria, Va.).

The coated specimens were examined in a JEOL SMU-3 scanning electron microscope manufactured by the Japan Electron Optics Laboratory Co., Ltd., Tokyo. An accelerating voltage of 25 kV was used throughout, and specimens were examined at magnifications ranging from 400 x to more than 20,000 x. Micrographs were obtained using Polaroid type 52 film.

Ignition Loss

Broken pieces from the tested cubes were collected, crushed mechanically, screened through a No. 8 sieve, treated with acetone to stop hydration, and placed in the oven at 105°C for overnight drying.

The equipment used to determine the loss on ignition consisted of a type H6T Mettler analytical balance, a set of three platinum crucibles, and an automatic muffle furnace. The analytical balance was read to one ten-thousandth of a gram. Approximately one gram of sample was weighed into each crucible, and the crucibles were introduced into the muffle furnace set at 1050°C for a period of two hours. The crucibles were then cooled in a dessicator for 40 minutes before making the final weighing.

The ignition loss values include a contribution representing ignition loss of the added admixtures. Ignition loss of the sulfonated lignin was separately determined to be 51% by weight. The CO_2 evolution for $NaHCO_3$ is equivalent to an ignition loss of 52% of its weight. In the pastes examined, $NaHCO_3$ was added in the proportion of 1.44% by weight of the cement, and the sulfated lignin was added at 0.84%. Applying the estimates of ignition loss expected for these components, a total weight loss of 1.1% would be expected for these components; the net ignition loss due to the hydrated cement paste per se was then taken as the measured ignition loss minus 1.1%.

Compressive Strength

The ASTM Designation:C 109-70 procedure was followed in essence. As mentioned previously, it was found necessary to make some additions to the cube molds to prevent leakage of the paste occurring, and the casting procedure used was also a little different from standard.

A sturdier base plate having means to be clamped to the 50.8 x 50.8 mm (2 x 2 in.) cube molds was substituted for the original base plate, and a thin non-absorbent rubber pad was glued on the top surface of the base plate to secure a leak-free fit between the cube mold and the plate when clamped together (see Figure 3).

All cube specimens were cast in two layers, and each layer vibrated for 10 seconds on a Syntron vibrating table set at 100 vibrations per second. Once cast, the cube molds were wrapped with plastic and a wet towel placed over them and kept in the laboratory until demolding.

A Forney hydraulic testing machine, type FT 40 DR, capacity 1.16×10^6 N (250,000 lb), was used to run the compressive strength tests. The rate of loading of the cubes was approximately 1.72 MPa/sec (250 psi/sec).

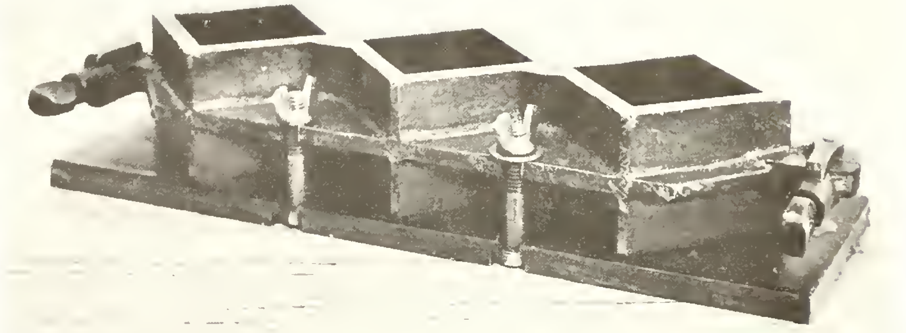

Figure 3. Cube Molds for Casting Cement Paste.

Pore Size Distribution

A 410 MPa (60,000 psi) mercury intrusion porosimeter, catalog No. 5-7125 D,-DE, manufactured by the American Instrument Company, Silver Spring, Maryland, was used for these tests.

Cement paste specimens having W:C ratio of 0.24 by weight, were specially made to determine their pore size distributions at different ages. The paste was cast in a single layer in a plastic container, which was then tightly sealed and kept in the laboratory 24 hours. After demolding, the paste was broken so as to produce five similar large pieces. These were placed in clean water for curing. At the desired age, individual pieces of cement paste were further broken in such a way as to obtain smaller pieces having fresh fracture surfaces and a suitable shape for the penetrometer space in which the sample is introduced for the test. The hydration process of the paste was then stopped with acetone and the sample placed in the 105°C oven, for 24 hours. The dry sample was cooled in a dessicator prior to test.

High pressure mercury intrusion in low porosity cement paste was carried out following a preset time and pressure schedule. At each pressure step the pressure was held long enough to allow intrusion equilibrium in the paste. As pressure in the system is increased mercury tends to contract and the oil surrounding the penetrometer (in which the sample and the mercury are enclosed) evolves heat and produces volume expansion of the mercury. Furthermore, as the pressure is held at each step for allowing intrusion equilibrium in the paste the temperature of the oil changes slightly and produces a volume change effect in the mercury. The net result of these volumes changes was evaluated by determining correction factors obtained from volume changes experienced by a blank test (carried out without cement paste but following the same preset time and pressure schedule). The true intrusion values of the paste were obtained by applying these correction factors to the actual intrusion readings.

Permeability Measurements

Low porosity cement pastes having W:C ratio 0.22, 0.30 and 0.35 were prepared in vacuum as described on page 23, cast into 50 ml. centrifuge tubes, and compacted on a Syntron vibrating table following a preset schedule to secure optimum uniformity of the paste. Twenty-four hours later, the paste was demolded and placed under lime-saturated water for curing. Three conventional Portland cement pastes having W:C 0.35, W:C 0.40 and W:C 0.50 were also prepared and cast in the above-mentioned way. At the desired ages, the pastes were taken out of the curing container, and disks 2.16 mm (.085 in.) thick were sawn (wet) perpendicular to the axis of the cylinder. These disks constituted the sample for the permeability test and were not allowed to dry out.

A diagram of the constant pressure permeameter apparatus is shown on Figure 4.

Essentially, the apparatus consists of a permeability cell in which the specimen is placed, a system to apply pressure, and a cathetometer for reading changes of water height caused by percolation of water through the sample.

Methods Used With Concrete

The concrete mixes of this investigation were made up of low porosity cement, coarse aggregate, fine aggregate, water, special sulfonated lignin, and $NaHCO_3$ (for details on materials, see page 9). Concrete mixes having W:C ratios 0.26, 0.28, 0.30 and 0.32 were investigated. All the concretes made but two were batched so as to have a cement factor (C.F.) of 8.0 bags per cu yd (450 Kg/m^3); one concrete had C.F. 7.0 bags per cu yd (390 Kg/m^3) and another one had C.F. 10.0 bags per cu yd (560 Kg/m^3). The coarse aggregate to fine aggregate volume proportions were 1:1 for most concretes, although some exploratory mixes had 0.45 to 0.55 and 0.55 to 0.45 volume ratios.

The sulfonated lignin content in the mixes used was varied from 0.57% up to 0.93% of the weight of cement; the $NaHCO_3$ range was from 0.80% to 1.60% of the weight of cement. Although all practical treatment combinations in this range were not run, some of the results might be useful as a part of a block if a design

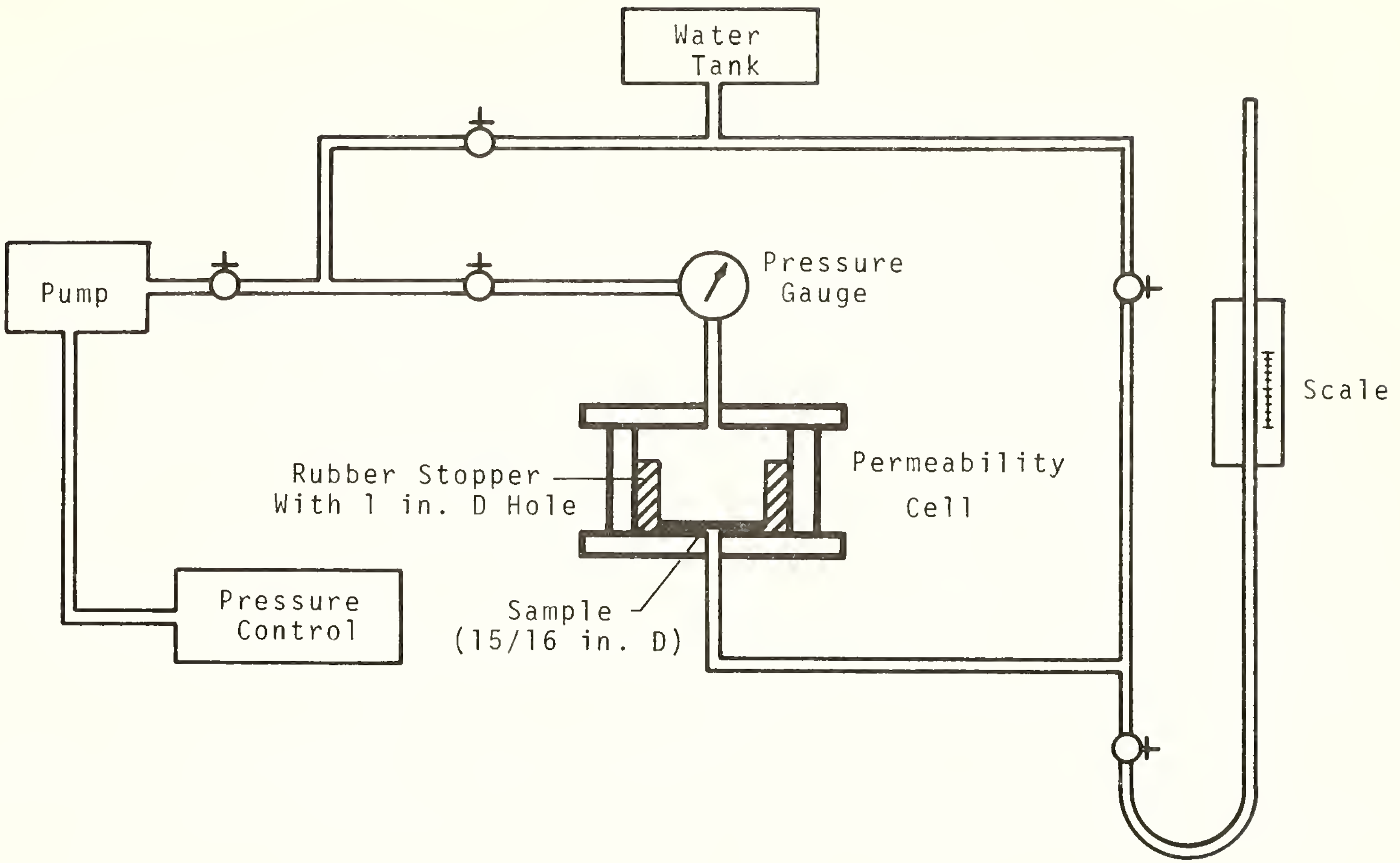

Figure 4. Permeameter Apparatus.

of this experiment were to be investigated in the future.

Details of Mixing

The ASTM Designation:C 192-69 procedure was followed in making the concrete mixes except for minor variations. A Lancaster SKG horizontal pan mixer, capacity 120 dm^3 (4.2 ft^3), manufactured by Posey Iron Works, Inc., Lancaster, Pa. was used to make all concretes. The order of mixing of the ingredient materials was: sand, gravel, absorption water, cement, and mix water containing the previously dissolved sulfonated lignin and $NaHCO_3$. The mix water solution containing the sulfonated lignin and $NaHCO_3$ was prepared in the same way as the corresponding one used in making cement pastes (see page 15). The absorption water did not contain either admixture.

The first step in each mixing operation consisted of "buttering" the mixing bowl. This was achieved by making a mortar having approximately the same proportions of that of the batch to be mixed (by hand) and spreading it over the mixer bowl and paddles.

Excess mortar was then removed and the fine aggregate placed in the bowl. The coarse aggregate was added on top of the fine, and all the aggregate was spread over the bowl. The mixer was then started and the absorption water poured onto the aggregates in the bowl. About one minute was allowed for absorption, then the cement was added and followed by the solution containing the dissolved admixtures. It took about 45 seconds to pour all the solution into the bowl. A three minute mixing period, beginning from the moment the solution was put in contact with cement, was followed by a waiting period of three minutes. During this period the mixer bowl was covered with wet burlap to minimize evaporation from the bowl. A final two minute mixing period was then carried out. Temperature and relative humidity in the laboratory were recorded for each mix. All concrete specimens were cast in two layers, each layer compacted by external vibration applied on the mold.

Slump

The slump test was run following the ASTM Designation:C 143-71 procedure except for the time at which the slump was measured. The slump changes with time over a 15 or 20 second period after the cone is lifted because of the peculiar rheological behavior of low porosity concrete. For this reason the slump reading was taken at a standard time of 30 seconds after lifting the cone.

Vebe Time

The Vebe time of the concrete was determined in accordance with the usual procedure as designated by the manufacturer. No ASTM standard method is prescribed.

Air Content

The air content in the freshly mixed low porosity concrete was determined by following the procedure described by ASTM Designation:C 231-72T. In this determination a Techkote-White meter (air meter), manufactured by Prestite Division, El Segundo, Ca., was used.

Compressive Strength

The ASTM Designation:C 39-72 procedure was followed to determine the compressive strength of the concrete. The size of the cylindrical specimens was 76.2 x 152.4 mm (3 x 6 in.). A Forney FT 40 DR testing machine, capacity 1.16 x 10^6 N (250,000 lb), manufactured by Forney's Incorporated, New Castle, Pa., was used to test the cylinders.

Flexural Strength

The flexural strength of the concrete was determined by following the procedure described by ASTM Designation:C 78-64. The size of the concrete beams was 76.2 x 101.6 x 609.6 mm (3 x 4 x 24 in.) and a 460,000 N (100,000 lb) Southwark-Emery testing machine manufactured by Southwark Foundry & Machine CO., Philadelphia, Pa., was used to run the tests.

Dynamic Modulus of Elasticity

The dynamic modulus of elasticity of the concrete was evaluated by determining the time taken by a pulse to travel along the length of the concrete specimen under test (ultrasonic pulse test), calculating the velocity of that pulse, and determining the dynamic modulus of elasticity of the concrete, E_d, from the equation

$$E_d = \rho V^2 \frac{(1+\mu)\ (1-2\mu)}{1-\mu}$$

where ρ = density of concrete, and μ = Poisson's ratio of concrete (14). A value of $\mu = 0.16$ was arbitrarily assigned as a reasonable estimate for the concrete tested.

The velocity of the ultrasonic pulse in the concrete was determined by using a V-scope, model C 4960, manufactured by James Electronics, Inc., Chicago, Il.; full-size concrete beams, 76.2 x 101.6 x 609.6 mm (3 x 4 x 24 in.), were used to run the test.

CHAPTER IV

RESULTS AND DISCUSSION

Rheology of Fresh Pastes and Concretes

Investigations were carried out on low porosity cement paste and concrete to study their rheological behavior in the fresh state. For cement paste, some attempts were made to determine actual viscometric behavior using a Brookfield rheometer and a number of qualitative observations were made during its handling. For concrete, the slumps and the Vebe times were measured, and qualitative observations on the handling characteristics were systematically obtained.

Cement Paste

A series of attempts were made to measure the rheological properties of the fresh low-porosity pastes using a Brookfield Rheolog viscosimeter equipped with helical path attachment and using a t-bar stirrer unit. Unfortunately, pastes of the W:C ratios employed in this work, while fluid, were too elastic and developed shear resistance far greater than the capacity of the instrument to properly record. In further experiments a rheological curve for a W:C 0.30 paste was determined (see Figure 5).

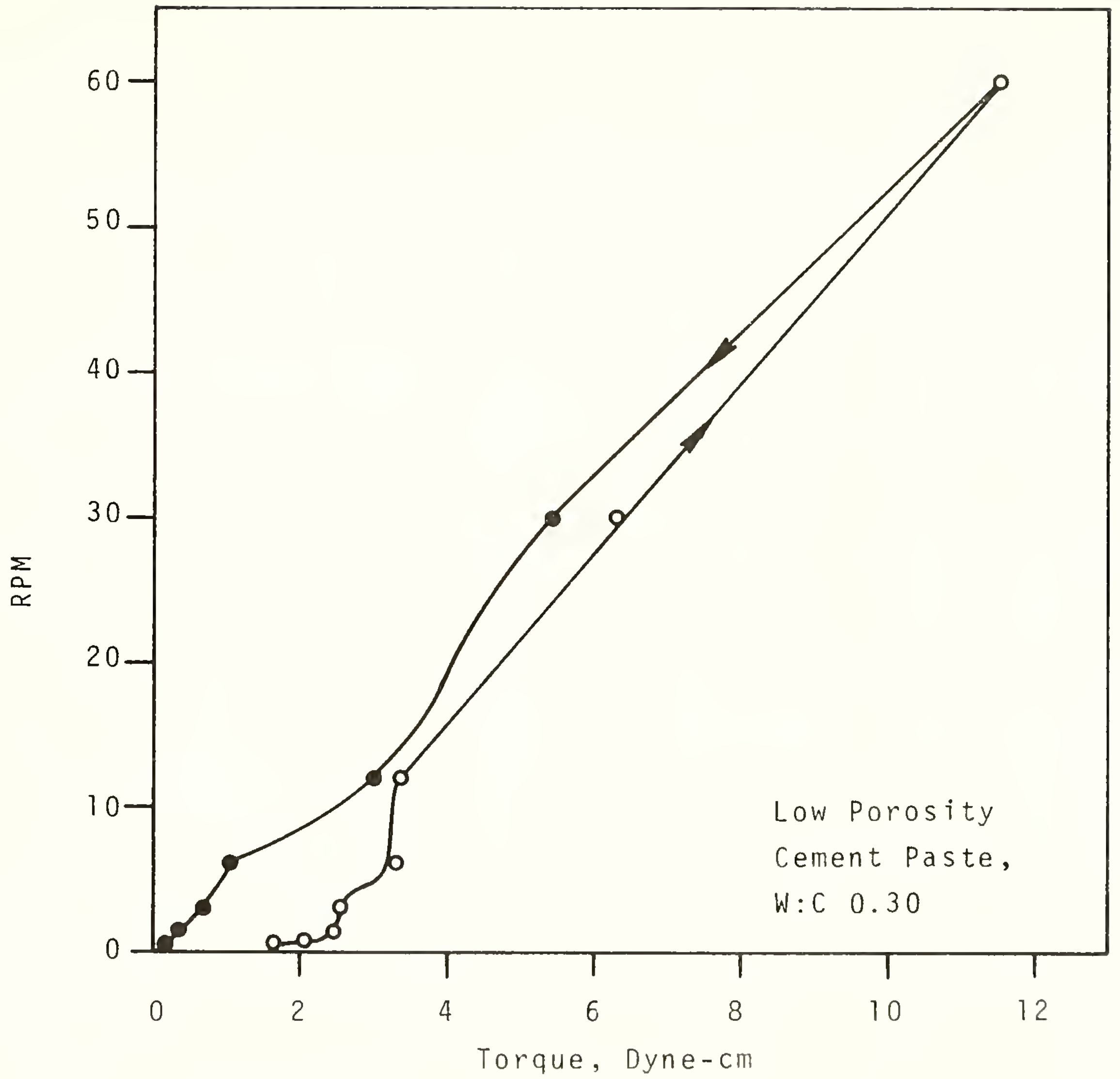

Figure 5. Rheological Curve of Low Porosity Cement Paste, W:C 0.30.

This paste showed complex behavior, but could be approximately described as a Bingham plastic fluid with a very low yield stress and an apparent plastic viscosity of the order of 1,900 centipoises.

The qualitative observations made on the rheology of low porosity cement paste can be summarized as follows:

Cement paste of W:C 0.24 flows very easy, with no other help than gravity; and might correspond to a consistency of 5 in the arbitrary scale adopted by Brunauer et al. (29).

Cement paste of W:C 0.23 flows easily when the mixing bowl is gently shaken with the palm of the hand; in the scale of Brunauer et al. it might correspond to a consistency of 4.

Cement paste of W:C 0.22 flows with some difficulty when the mixing bowl is gently shaken but flows easily when vibration is applied to it; in the scale of Brunauer et al. it might correspond to a consistency of 3.

Concrete

For low porosity concrete, the effects of some variables on the rheological response were investigated and the results are summarized in Table 3.

The figures and descriptions in the table are representative of the normal behavior of many replicates. All of the concrete mixes had a cement factor of 8.0 bags per cu yd (450 Kg/m^3) and an aggregate to cement ratio

Table 3. Influence of Some Variables on the Rheological Properties of Low Porosity Concrete.

Concrete Mix	W:C Ratio	Sulfonated Lignin Content, % Wc*	$NaHCO_3$ Content, % Wc*	Slump, mm(in.)	Vebe Time, Sec.	Workability	Air Content, %
1	.26	.84	1.44	205 (8.0)	11	Fair	4.0
2	.28	.84	1.44	205 (8.0)	5	Good	4.0
3	.30	.84	1.44	Collapse	Zero	Excellent	4.0
4	.32	.84	1.44	Collapse	Zero	Excellent	--
5	.28	.93	1.44	240 (9.5)	5	Good	4.2
6	.28	.75	1.44	240 (9.5)	3	Good	3.8
7	.28	.66	1.44	230 (9.0)	5	Good	3.8
8	.28	.57	1.44	40 (1.5)	11	Poor	--
9	.28	.70	0.80	230 (9.0)	5	Good	3.0
10	.28	.70	1.00	205 (8.0)	4	Good	3.4
11	.28	.70	1.40	190 (7.5)	7	Fair	2.5
12	.28	.70	1.60	90 (3.5)	8	Poor	--
13	.28	.70	1.20	Collapse	Zero	Excellent	3.0

* % Wc means percent of the weight of dry cement.

between 4.0 and 4.3 except for concrete mix No. 13, which had a cement factor of 10.0 bags per cu yd (560 Kg/m^3) and an aggregate to cement ratio of 3.0. In most of the concretes the coarse to fine aggregate volume proportion was 0.50:0.50; in some exploratory mixes this proportion was 0.45:0.55 and 0.55:0.45.

The adjectives under the heading "workability" attempt to describe the overall combined responses of the concrete to shoveling, compaction, pumping, and finishing, and its behavior with respect to working time, segregation and bleeding.

The effect of variation of the W:C ratio may be seen by comparing concrete mixes 1, 2, 3, and 4. W:C 0.30 or greater produce excellent concrete with respect to workability; good concrete is produced using W:C 0.28, but further reduction in the W:C does not produce an easy-to-work concrete mix. Skalny et al. (23) reported workability problems in low porosity concrete having W:C 0.30 or lower; the Vebe times measured for their concretes were excessively long (as long as three minutes). As a general comparison, Hattori and Yamakawa (11) obtained slump measurements of 225 mm (8.9 in.) for concretes having W:C 0.30 and W:C 0.32 batched with category B superplasticizing admixture (6). It should be mentioned, however, that the slump test by itself is not a good indicator of the workability of concrete, as can be deduced from Table 3.

The effect of the sulfonated lignin content on the workability of low porosity concrete can be appreciated by analyzing the results for concrete mixes 5, 6, 7 and 8. Easily workable concrete mixes can be made by using sulfonated lignin contents of 0.66% or greater; the optimum content for workability may be close to 0.75%, as judged by the best slump-Vebe time-workability combination. A concrete mix of poor workability was obtained when the sulfonated lignin content was reduced to 0.57% of the weight of cement, and the effective working time was much reduced.

The effect of varying the content of $NaHCO_3$ can be seen by comparing the results for concrete mixes 9, 10, 11 and 12. The sulfonated lignin contents in these mixes were kept constant at 0.70%, which was estimated to be optimal in terms of both workability and compressive strength. Readily workable concrete was obtained for $NaHCO_3$ contents of 0.8% and 1.0%, but $NaHCO_3$ contents of 1.4% and 1.6% produced concretes of only fair and poor workability, respectively. From the data in Table 3 it is difficult to estimate an optimum $NaHCO_3$ content, but the writer thinks that it may be close to 1.0%.

The effect of cement content in low porosity concrete on its workability was only briefly investigated. All of the concretes listed in Table 3 were prepared at a cement factor of 8.0 bags per cu yd (450 Kg/m^3) except concrete No. 13, which had a 10 bags per cu yd (560 Kg/m^3) cement factor. In addition, several trial batches with a cement factor of 7.0 bags per cu yd (390 Kg/m^3) were prepared, but this proved to have a relatively low slump (51 mm or 2 in.), and a relatively long Vebe time (11 seconds), and more important, it did not flow under vibrations in the usual way.

As seen in Table 3, low porosity concrete prepared with a cement factor as large as 10.0 bags per cu yd (560 Kg/m^3) undergoes complete collapse in the slump test and has a Vebe time of essentially zero, that is, it flows too rapidly to measure. Despite the extraordinary rheological behavior of this concrete, no segregation was observed to take place.

It appears from these results that the fluidity of the concrete increases markedly with the cement factor. Concretes made at cement factors of about 8.0 bags per cu yd are sufficiently fluid to have almost ideal working properties, and of course could be more economical than richer mixes that show complete collapse.

This relationship of increased fluidity at higher cement contents is also characteristic of conventional Portland cement concretes and concrete made with superplasticizers. Hattori and Yamakawa (11) indicated that for the same dosage of superplasticizing admixtures more workable mixes were obtained at the higher cement contents.

Little or no segregation was observed to occur in low porosity concrete, within the 0.26 - 0.32 W:C ratio investigated. Segregation problems have been reported in concrete made with superplasticizers, at least high W:C ratios (3). The presence of large voids as those seen in Figure 6 were not uncommon but did not produce any noticeable effect on the strength of the concrete.

The useful working time of the low porosity concretes reported here is of the order of 30 - 60 minutes. Longer working times were observed for higher W:C ratios and for higher sulfonated lignin:$NaHCO_3$ ratios. Concrete made with superplasticizers can be worked for longer periods (6).

Hydration of Low Porosity Cement Paste

The course of the hydration reactions in low porosity cement pastes were followed by studying temperature evolution rate, degree of hydration at various ages, and changes in internal structure at different stages in the hydration process. These aspects will be covered partly in this section and partly in the following section.

Temperature Evolution

This was determined with a device developed by Professor D. N. Winslow and described in page 20.

A typical temperature evolution curve of low porosity cement paste is plotted in Figure 7. Similar curves were

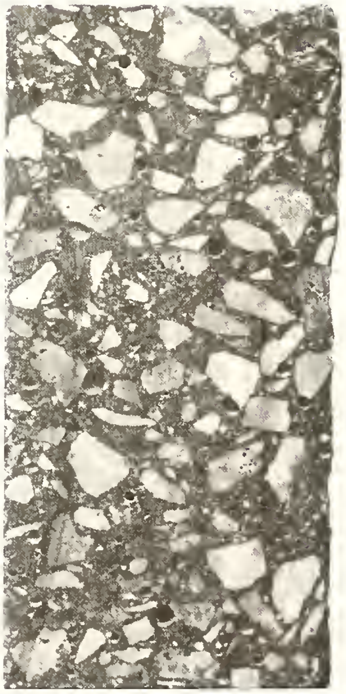

Figure 6. Cross Section View of 76.2 x 152.4 mm (3 x 6 in.) Hardened Low Porosity Concrete Cylinder, W:C 0.30.

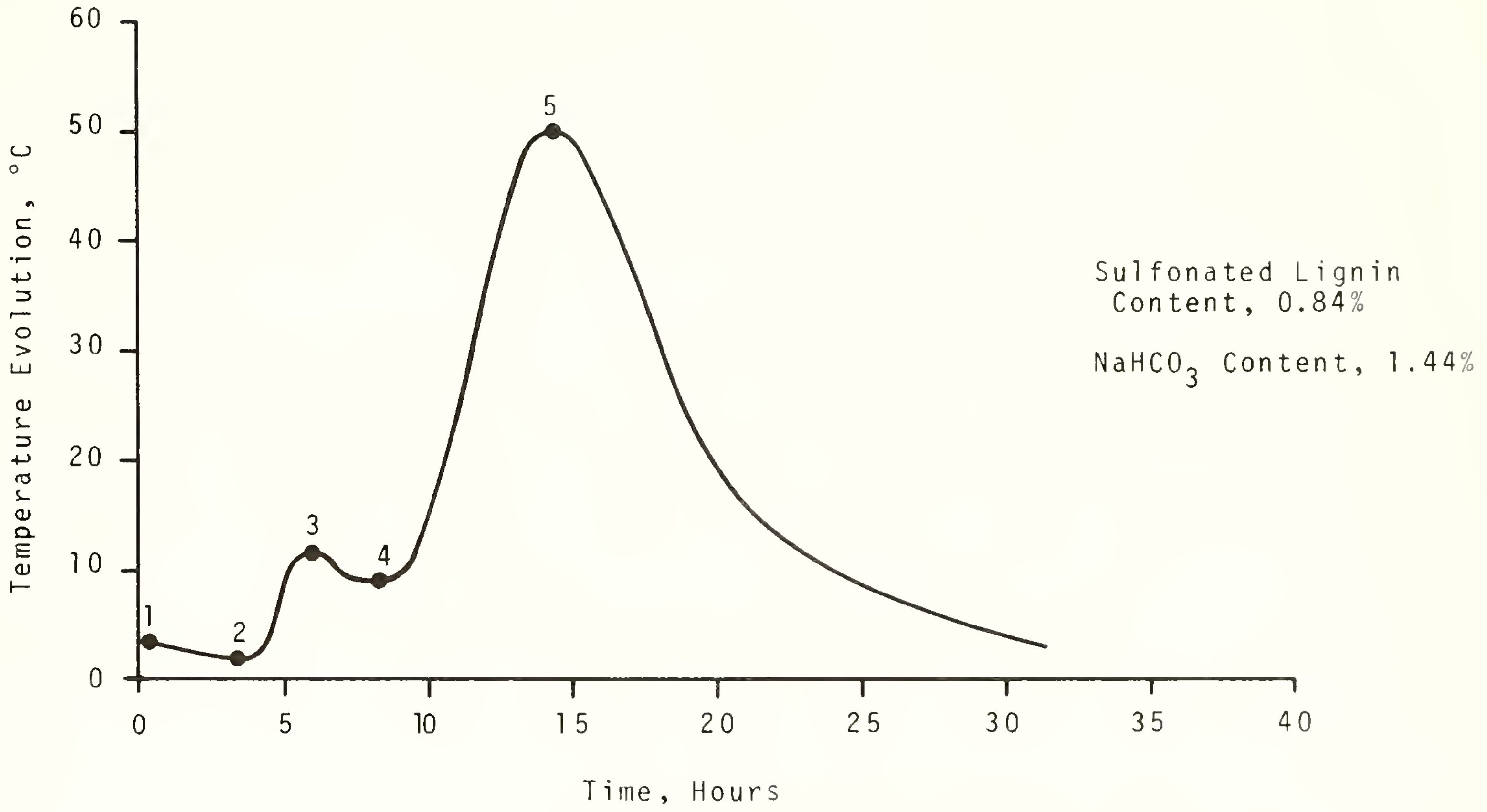

Figure 7. Temperature Evolution Curve of Low Porosity Cement Paste.

obtained for all of the W:C ratios tested. Except for the hump between points 2 and 4, this curve is similar to corresponding curves evolved during the hydration of a conventional cement paste as indicated in Figure 8 from (24). The curve of Figure 7 is similar to heat evolution curves previously described (24). Brunauer et al. (5) divided the hydration process taking place with low porosity cement pastes into three stages. Stage I included the pre-dormant period and the dormant period, and included effects of all the reactions that occur between the time of first contact between water and cement and the time the dormant period ends (see Figure 7). Not much heat is evolved during this stage. Subsequently, in Stage II, the reaction rate speeds up and considerable heat is evolved as indicated in Figure 7. In the present work a double temperature rise effect was observed within this stage, presumably due to some retarding effect of the admixtures used. In Stage III the heat evolution rate in the paste decreases continuously; this corresponds to the right side of the curve in Figure 7 after point 5.

The effect of the W:C ratio on the temperature evolution rate curve for low porosity pastes is presented in Table 4. The quantities tabulated represent mean and standard diviation of the temperatures and times for the attainment of points 1, 2, 3, 4 and 5 as indicated in

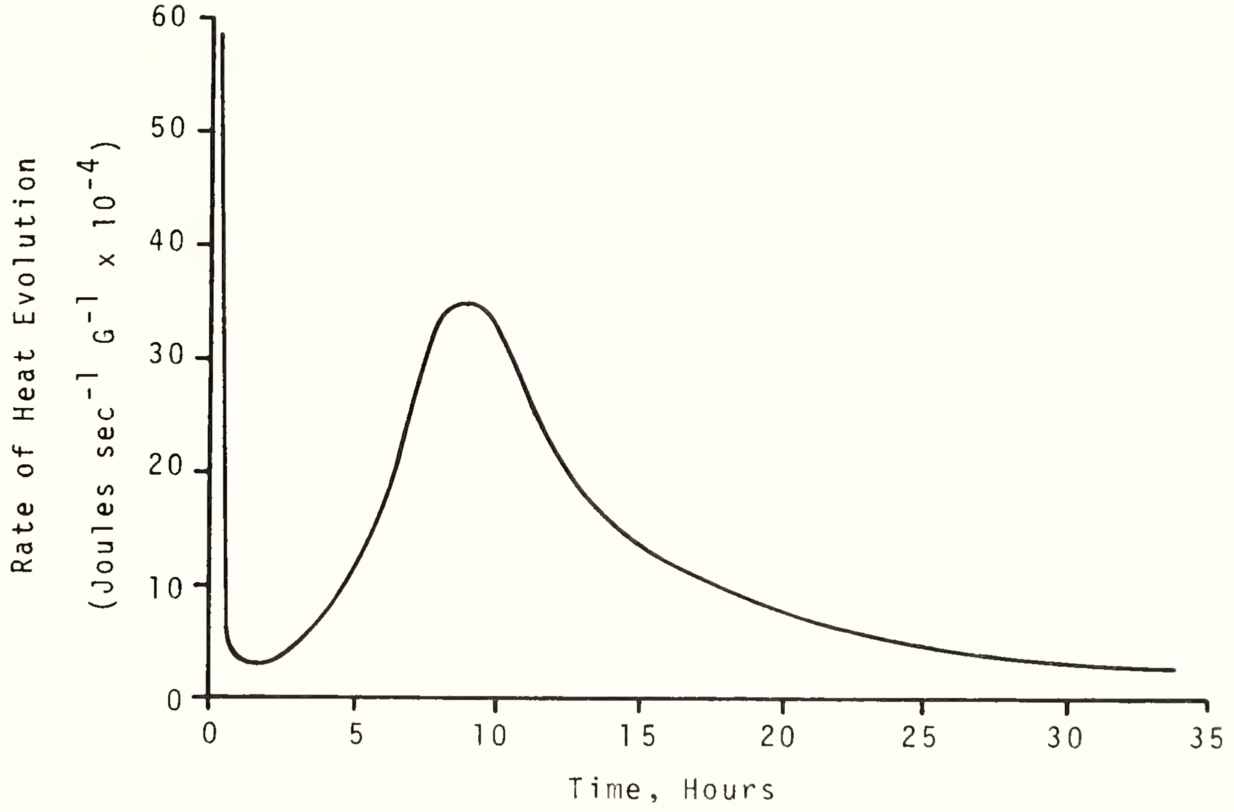

Figure 8. Heat Evolution Rate Curve of Ordinary Portland Cement Paste. (From Reference 24).

Table 4. Effect of Water to Cement Ratio on the Temperature Evolution of Low Porosity Cement Paste.**

Hydration Stage	Point on Curve of Figure 7	W:C 0.22 Time, Minutes $\bar{X} \pm \sigma$	W:C 0.22 Temperature Elevation,* °C $\bar{X} \pm \sigma$	W:C 0.23 Time, Minutes $\bar{X} \pm \sigma$	W:C 0.23 Temperature Elevation,* °C $\bar{X} \pm \sigma$	W:C 0.24 Time, Minutes $\bar{X} \pm \sigma$	W:C 0.24 Temperature Elevation,* °C $\bar{X} \pm \sigma$
I	1	5	3.5 ± 0.6	5	3.8 ± 0.5	5	3.8 ± 0.8
---	2	200 ± 35	2.5 ± 0.6	220 ± 30	2.3 ± 0.5	445 ± 65	1.2 ± 0.8
II	3	370 ± 80	10.9 ± 2.3	360 ± 25	12.2 ± 1.6	910 ± 145	9.2 ± 2.5
	4	505 ± 85	8.5 ± 1.4	500 ± 65	9.2 ± 1.2	1025 ± 140	8.2 ± 1.7
---	5	865 ± 95	47.8 ± 4.2	865 ± 85	50.8 ± 3.0	1400 ± 140	50.5 ± 3.0
III							

** Sulfonated Lignin Content, 0.84%; $NaHCO_3$ Content, 1.44%.

* Above the Initial Temperature, 24°C.

Figure 7 from six replicate determinations at each W:C ratio. The degree of temperature elevation attained by the paste at any stage of hydration is practically independent of its W:C ratio, at least in the W:C ratio range examined. However, the times required to reach points 2 and 3 on the curve of Figure 7 are longer for higher W:C ratios, particularly in the case of the W:C 0.24 paste. Once the point 3 maximum has been reached, the additional times required to reach the point 4 minimum and the point 5 maximum are practically independent of the W:C ratio of the paste.

At any given W:C ratio, the sequence of changes in the temperature of the paste indicated in Figure 7, once initiated by the attainment of the first minimum corresponding to point 2, was highly repeatable with respect to both temperature maxima and minima and with respect to time relative to that of point 2. However, under laboratory conditions it was observed that the variation between replicates consisted largely of variation in the time it took to complete Stage I, i.e., to reach point 2.

In particular, it was observed that if the ambient RH of the laboratory air was higher than 75% RH, the completion of Stage I and the attainment of the minimum in temperature marking point 2 was delayed, in one case for as long as about 46 hours. As indicated in the next section, attainment of this stage is associated with the phenomenon of set, and in the case mentioned, set was also correspondingly delayed.

Time of Setting

Determinations on the time of setting were made on seven low porosity cement pastes: two on pastes having W:C 0.22; three on W:C 0.23 pastes; and two on W:C 0.24 pastes. Part of the specific cement paste preparation that was used to determine its time of setting was used to determine its temperature evolution upon hydration. It was then possible to correlate the time of setting of the paste to its corresponding position on the temperature evolution curve being recorded. It was found that setting time, as measured by the Vicat needle penetration, coincided with the attainment of the first minimum in the temperature evolution curve (i.e., point 2 in Figure 7) within 10 minutes or less.

In addition to the tests described above, a series of eleven replicate determinations of the temperature evolution curves were carried out.

There was some small variation between setting times measured by the Vicat method for replicate cement pastes. In addition, the attainment of the corresponding minimum in the temperature evolution curves for the additional samples showed some variation among themselves. All of the data obtained are summarized in Table 5. It is seen

Table 5. Time of Setting of Low Porosity Cement Paste.

W:C Ratio	Time of Set, Minutes as Determined by Vicat Method (Min.)	Average	Time to Reach First Minimum in Temperature Evolution Curve, (Min.)	Average
0.22	160	200	160*	200
	240		240*	
			180	
			240	
			210	
			160	
0.23	200	215	200*	220
	220		220*	
	220		220*	
			275	
			180	
			220	
0.24	480	435	480*	445
	390		390*	
			480	
			510	
			360	
			--	

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* Specimens for which both types of measurement were made.

that there is little increase in the time of setting of the W:C 0.23 paste as compared to that of the W:C 0.22 paste; however, the time of setting of the W:C 0.24 paste is considerably longer.

Earlier it was remarked that if the ambient RH of the laboratory air exceeded 75%, the attainment of the minimum corresponding point 2 on the temperature evolution curve (Figure 7) was delayed. It was also observed that a corresponding delay in setting time took place. All of the data given in Table 5 were for pastes mixed when ambient RH was close to 50% - 60% (as indicated by sling psychrometer measurements) and hence were not subject to delayed set.

The cause of the delay in set (and associated delay in the temperature evolution pattern) associated with high ambient RH levels is not known, but obviously reflects a changed pattern of early hydration reaction under these conditions.

Degree of Hydration

Normally the degree of hydration of a cement paste is estimated by assessing the amount of water chemically combined with the hydration products.

The degree of hydration is usually expressed by the relation

$$X = \frac{W_n}{W_n^\circ} \times 100$$

where:

W_n° = chemically combined water at 100% hydration of the cement per gram of the original cement, and

W_n = non-evaporable water of the cement paste at the age of test.

In the present study, as previously indicated in Chapter III, the admixtures used are themselves subject to ignition loss, and it was calculated that such loss would amount to 1.1% of the ignited weight. This amount was then subtracted from the experimentally determined ignition loss to provide our best estimate of W_n.

However, evaluation of W_n° has proven to be difficult. This parameter is often determined by allowing the cement concerned to hydrate at a high W:C ratio (usually 10) in a rotating chamber so that the reaction would be encouraged to procede to completion. The hydrating cement is sampled periodically and loss on ignition determined. The process is continued until the loss on ignition shows no further increase with additional time of hydration, whereupon the hydration process is considered to be complete, and the equilibrium value for the ignition loss is designated W_n°. Values of W_n° for hydrated Portland cements typically range between 21% and 23%.

Brunauer et al. (29) reported a value for W_n° of 22.1% for the Type I cement and 19.6% for a Type II cement used in formulating his low porosity cements.

Details of the method of determination were not given.

In the present study an attempt was made to determine W_n° using a hydrating mixture of composition as follows: 50 g ground clinker, 0.42 g of sulfonated lignin, 0.72 g of $NaHCO_3$, and 500 ml H_2O, placed in continuous rotation. At approximately 4 weeks a sample yielded an ignition loss of 17%; however, a sample taken at 9 weeks yielded a value in excess of 31%, and subsequent samples indicated an equilibrium value of 29%.

Because these values are far in excess of reasonable estimates of W_n°, it is felt that calculations of the degree of hydration using this value as representing 100% hydration would yield erroneously low results. A possible explanation for the discrepancy might be the formation of unusually water-rich hydration phases in this system.

For the purpose of forming a reasonable estimate of the degree of hydration, the value quoted by Brunauer et al. for their Type I cement, 22.1%, was used as W_n° for the low porosity cement of the present investigation.

The degree of hydration calculated in the basis of ignition loss corrected by the 1.1% estimated loss due to the admixtures and divided by 22.1% (as W_n°) are given in Table 6. The resulting data are plotted in Figures 9 and 10. The results indicate that the degree of hydration of the paste at any given age is slightly

Table 6. Ignition Loss Data and Estimated Degree of Hydration of Low Porosity Cement Paste.

Time	W:C	Ignition Loss	Net Ignition Loss	Est. Degree of Hydration, %
6 1/2 Hrs. (Setting time)	0.24	3.4	2.3	10
15 Hrs.	0.22	4.8	3.7	17
	0.23	5.6	4.5	20
	0.24	4.8	3.7	17
21 Hrs.	0.22	4.7	3.6	16
	0.23	4.7	3.6	16
	0.24	4.3	3.2	15
24 Hrs.	0.22	6.3	5.2	24
	0.23	5.3	4.2	19
	0.24	6.5	5.4	24
2 Days	0.22	11.2	10.1	46
	0.23	11.8	10.7	48
	0.24	12.1	11.0	50
3 Days	0.22	11.7	10.6	48
	0.23	12.3	11.2	51
	0.24	13.7	12.6	57
7 Days	0.22	12.4	11.3	51
	0.23	13.1	12.0	54
	0.24	14.1	13.0	59
28 Days	0.22	13.6	12.5	57
	0.23	14.7	13.6	62
	0.24	14.8	13.7	62
90 Days	0.22	14.1	13.0	59
	0.23	14.5	13.4	61
	0.24	14.9	13.8	62

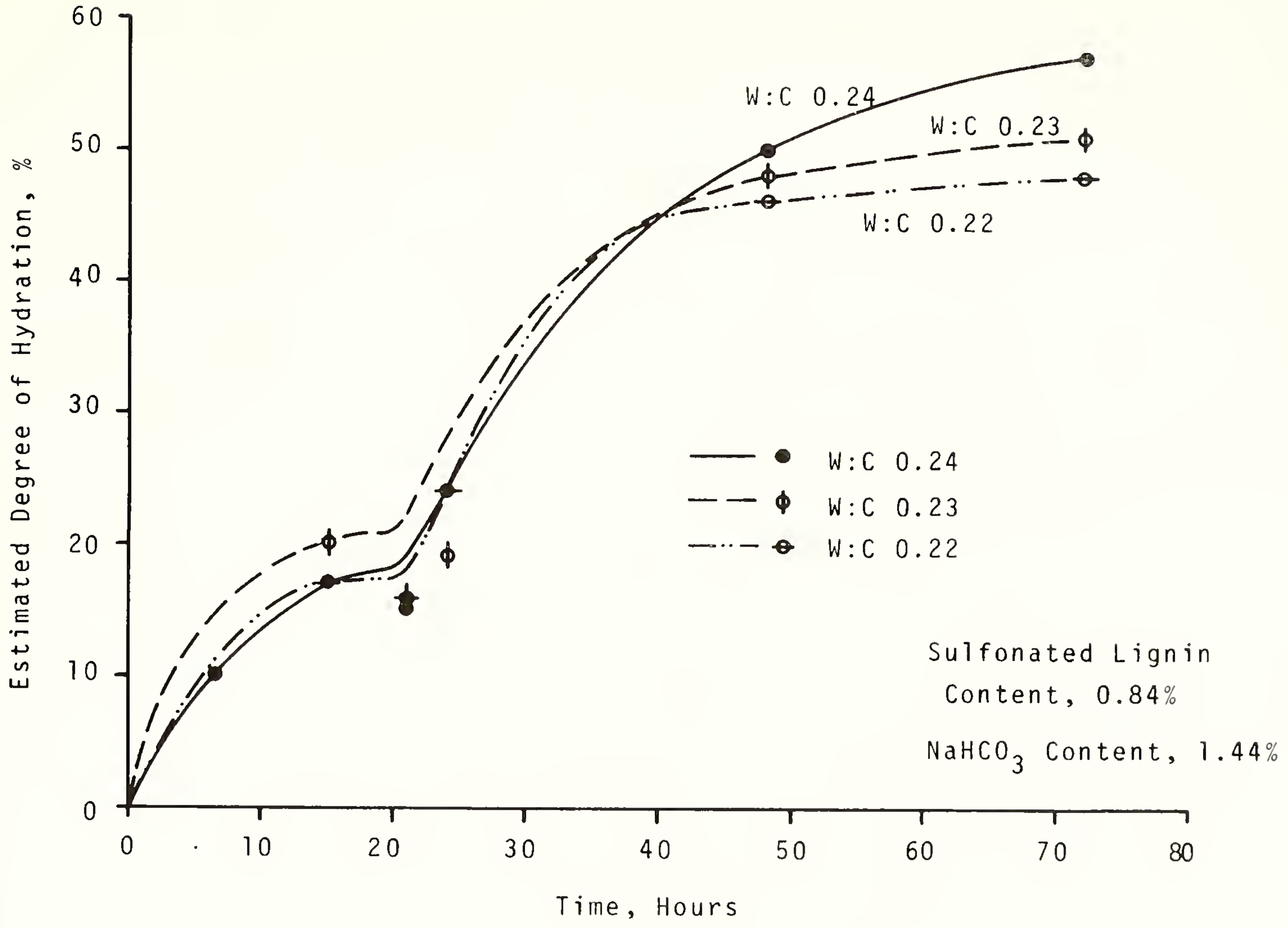

Figure 9. Degree of Hydration of Low Porosity Cement Paste at Early Ages.

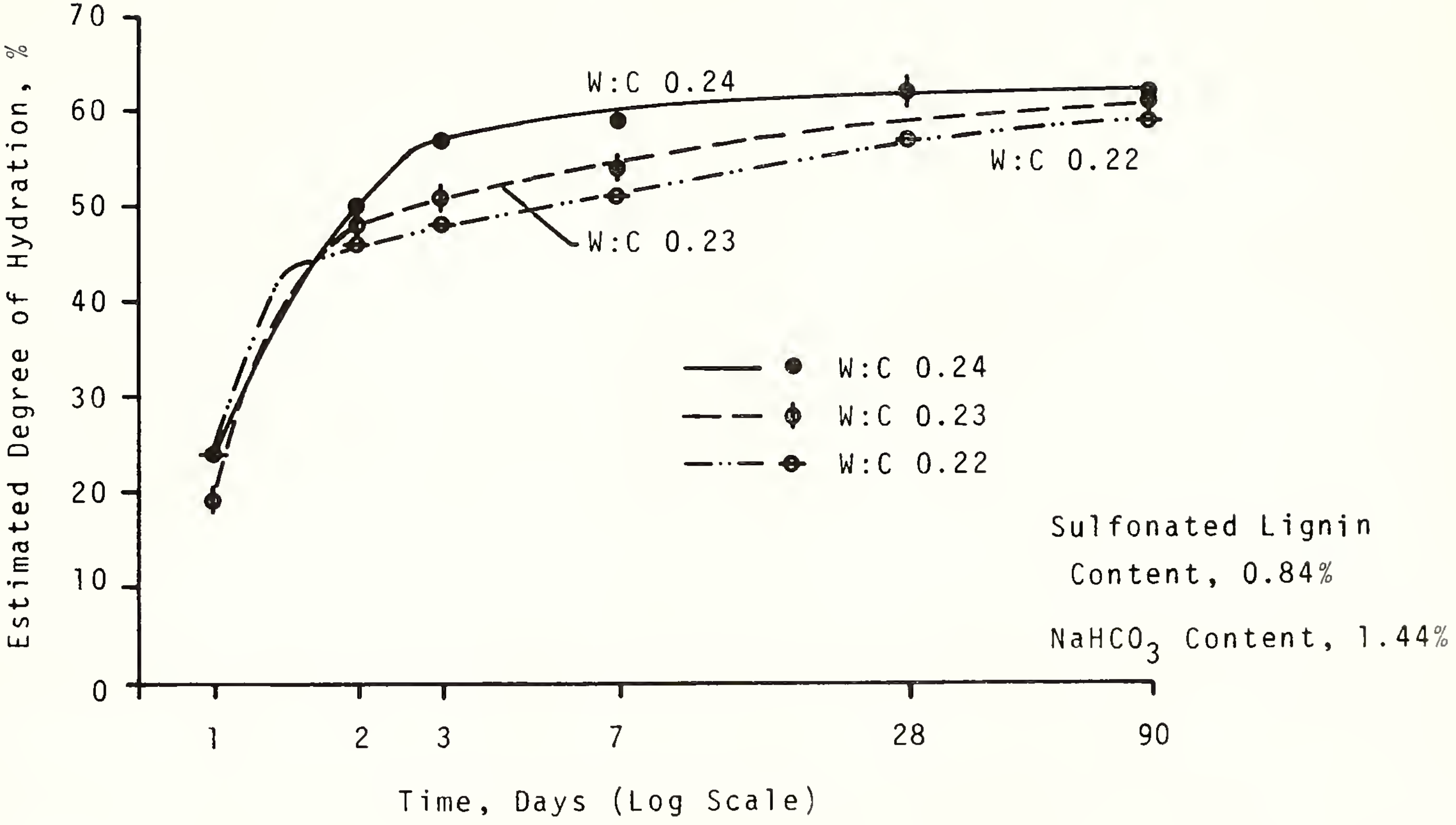

Figure 10. Degree of Hydration of Low Porosity Cement Paste.

higher for higher W:C ratios. At two days of hydration, the pastes have reached a degree of hydration of about 80% of that value reached by the corresponding 90-day old paste. Brunauer et al. (18) found that the degree of hydration of a Type I Portland cement clinker having W:C 0.20 at 90 days of hydration was close to 65%; this is slightly higher than the corresponding values obtained here, but the pattern of hydration vs. time was similar to the present results.

Microstructure of Low Porosity Cement Paste

Combinations of three investigation techniques, scanning electron microscopy (SEM), differential thermal analysis (DTA), and x-ray diffraction (XRD) were used to study the microstructure and composition of low porosity cement paste. Details of the composition will be discussed in the following sections.

Hardened low porosity cement paste is composed mostly of colloidal particles of complex composition, partially hydrated cement grains, and crystals of calcium hydroxide. Figure 11 represents the appearance of the ground clinker. The specimen was prepared by coating a stub with a mixture of silver dag and Duco cement and inverting over a bed of dry cement grains. Loose cement grains were removed by use of a compressed freon "duster" and the specimen dried and coated in the usual fashion. The particles are mostly in the 0.5 μm and above size

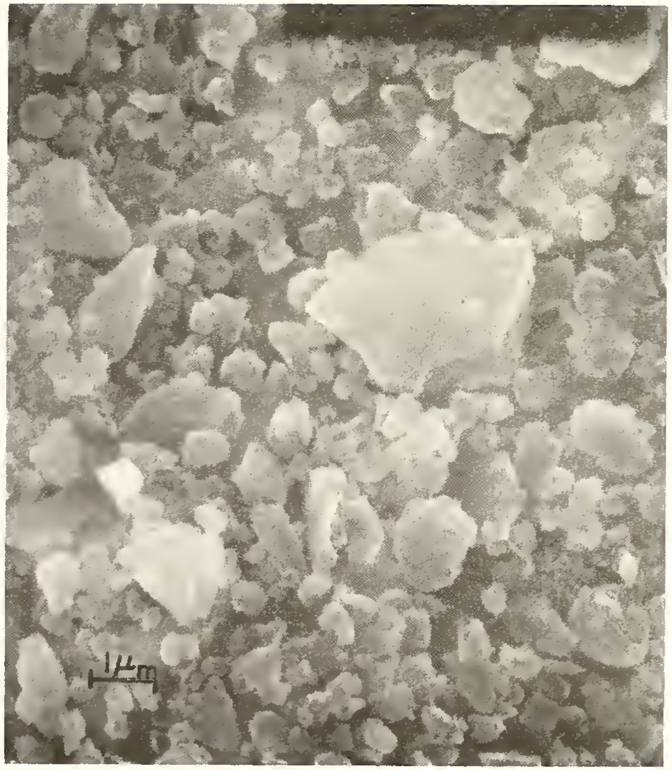

Figure 11. SEM Micrograph. Ground Unhydrated Clinker. (x 7000)

Figure 12. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at Two Hours. (x 4000)

range, and are multifaceted equant grains having sharply-defined edges. In this preparation the particles are not packed very tightly. Occasional larger grains of the order of 15 µm or more were also observed but not pictured.

The earliest stages of hydration, corresponding to the period up to the time of set (and to point 2 on the temperature evolution curve of Figure 7) did not produce any obvious collection of hydration products. Figure 12 represents a view taken at 2 hours, and shows a large cement grain with a partial coating of smaller grains, some of which may represent hydration product.

The appearance of the pastes at the time of setting (6 $^1/_2$ hours) is indicated by Figures 13 and 14. Again, essentially all of the grains observed are apparently cement grains, and little visible hydration product seems to have been formed. Based on a special ignition loss determination for this sample, the estimated degree of hydration at this stage was about 10%.

At 15 hours, the overall appearance of the cement pastes have changed considerably, as indicated in Figure 15. Much hydration product has formed between 6 hours and 15 hours, and appears as finer-texture coatings over residual cement grains and as clusters of particles in the space between grains.

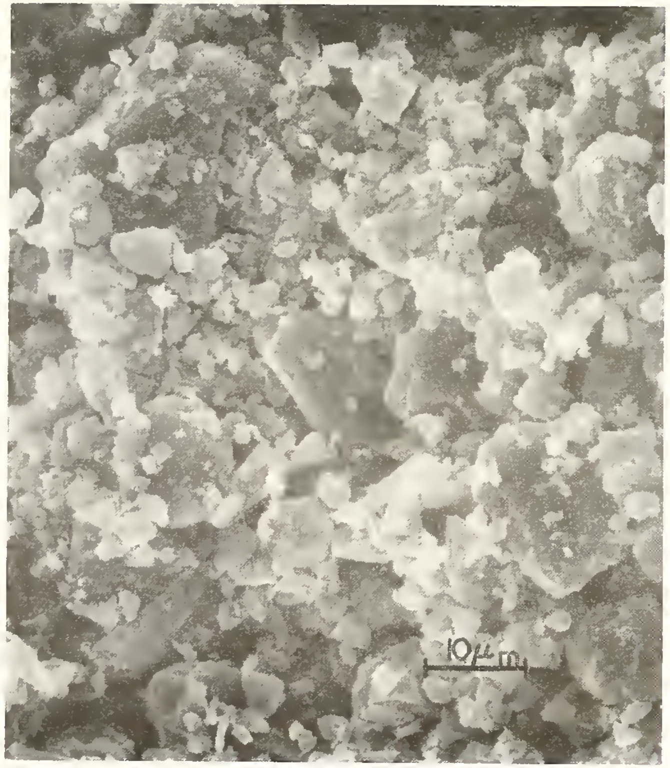

Figure 13. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at Setting Time. (x 1500)

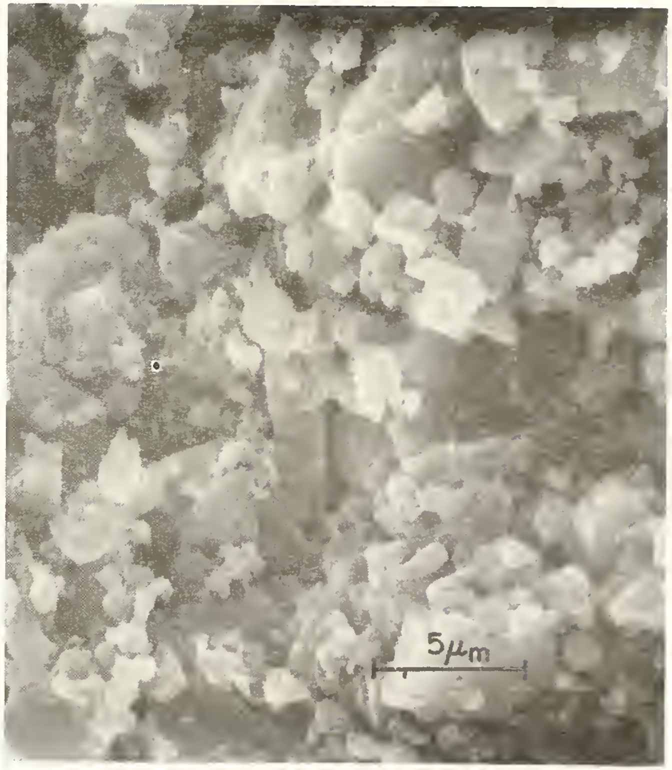

Figure 14. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at Setting Time. (x 4000)

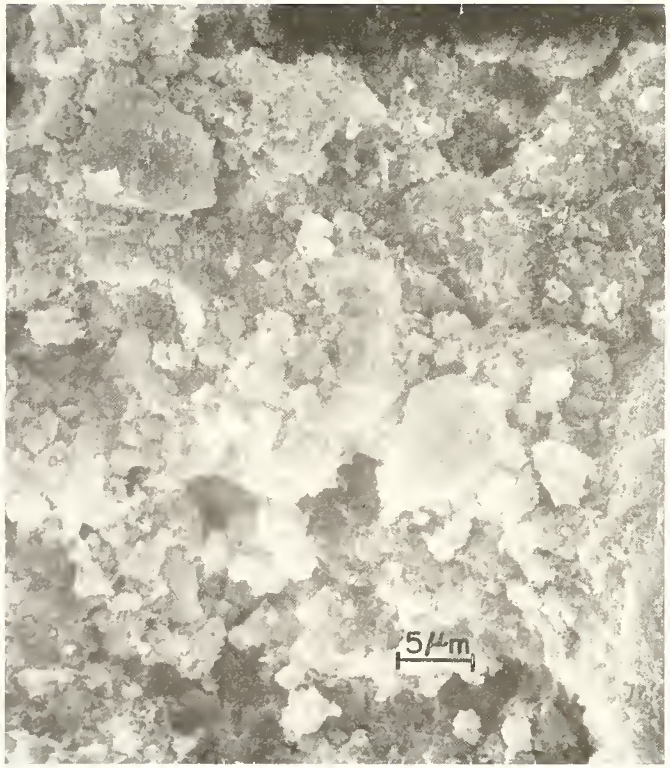

Figure 15. SEM Micrograph. Microstructure of Low Porosity Cement Paste, W:C 0.22, at 15 Hours. (x 2000).

Figure 16. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at 15 Hours. (x 3000).

At slightly higher magnification the appearance of the hydration products can be seen more clearly. (Figure 16). They appear to be primarily thin plates, some of which are seen on edge as bright lines of the order of 1 to 2 μm in length. In addition in Figure 16 a few flattened elongated hydration product particles can be seen (bottom left portion). A similar view with additional detail is shown in Figure 17. A higher magnification view illustrating the thinness of some of the platy products and also the character of the elongated particles is shown in Figure 18. Further hydration of the cement paste results in greater accumulation of hydration products and a more closely packed structure. An overall view of the microstructure at 24 hours is shown in Figure 19.

At this stage it has become difficult to detect obvious residual cement particles. Most of the cement grains have either hydrated completely or have become covered with hydration products so that their outlines are no longer apparent.

The individual hydration product particles are still mostly distinguishable at this stage, as indicated in the higher magnification views of Figures 20, 21 and 22. These micrographs indicate that there are three structural types present: small relatively non-descript but equidimensional grains of the order of 0.5 μm or less,

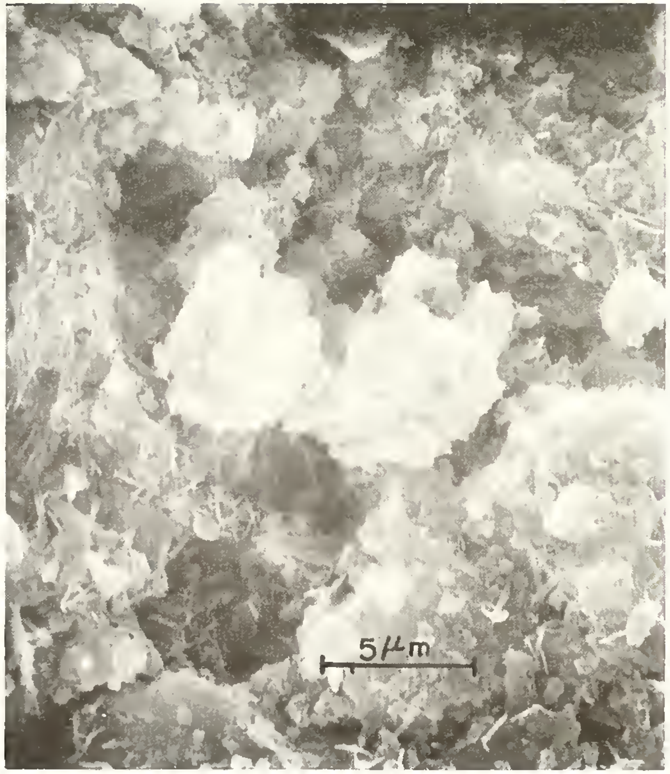

Figure 17. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at 15 Hours. (x 4000).

Figure 18. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at 15 Hours. (x 10000).

Figure 19. SEM Micrograph. Microstructure of Low Porosity Cement Paste, W:C 0.24, at 24 Hours. (x 1500).

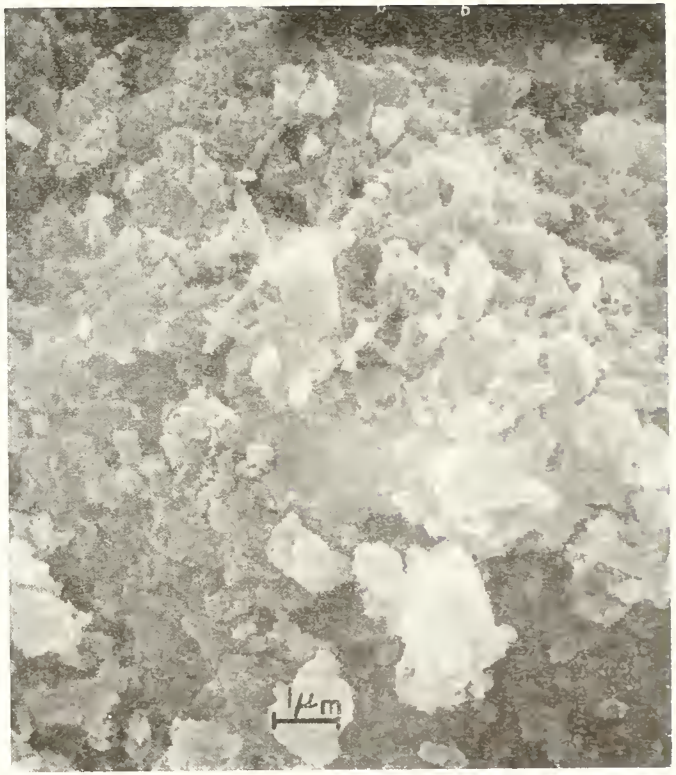

Figure 20. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 24 Hours. (x 7000).

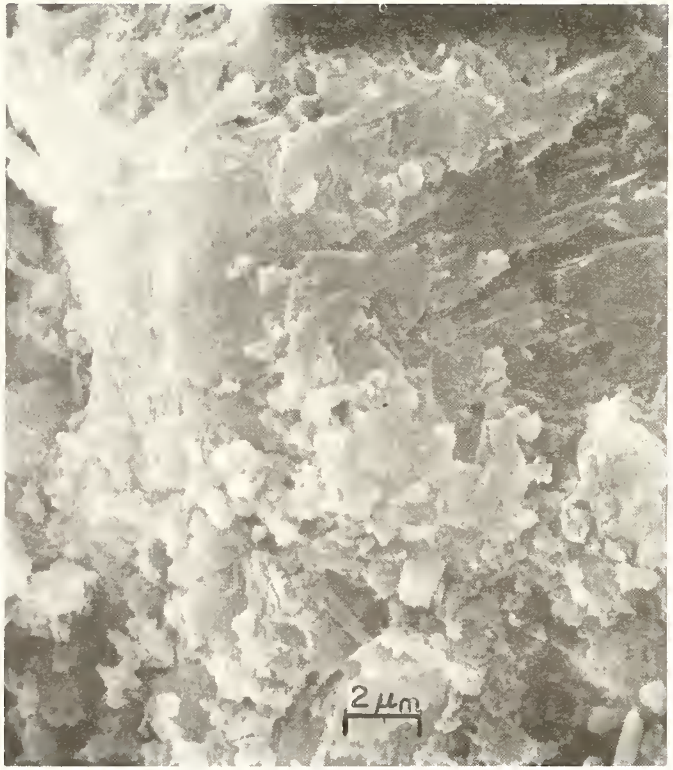

Figure 21. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 24 Hours. (a) (x 5000).

Figure 22. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 24 Hours. (b) (x 5000).

probably corresponding to the Type III C-S-H product as classified by Diamond (8); a few elongated particles of the type mentioned earlier; and areas of dense, even-gray tone that are much larger in size and correspond to lime crystals or regions of gel that have been infiltrated or covered over with lime deposits.

At 36 hours, as indicated in Figure 23, there is a continued trend to what might be described as "fusion" of hydration products. It is less easy to detect individual grains or particles of hydration product, although in some areas one can still do so; small equidimensional (Type III) grains are visible in Figure 24, and a few elongated particles are still visible in Figure 25. However, most of the hydration products are now in relatively cemented or fused clusters of the order of 10 μm or more. As can be seen in Figure 25 and more clearly in Figure 26, there is still considerable void space visible between the clusters.

As indicated in the hydration curve of Figure 10, by 2 days most of the hydration that will occur has already taken place. The resulting microstructure has become nearly (but not completely) fused into a massive structure with comparatively little visible residual pore space, as indicated in Figure 27, which is a representative area taken at low magnification.

Figure 23. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at 36 Hours. (x 2000).

Figure 24. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at 36 Hours. (a) (x 3000).

Figure 25. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at 36 Hours. (b) (x 3000).

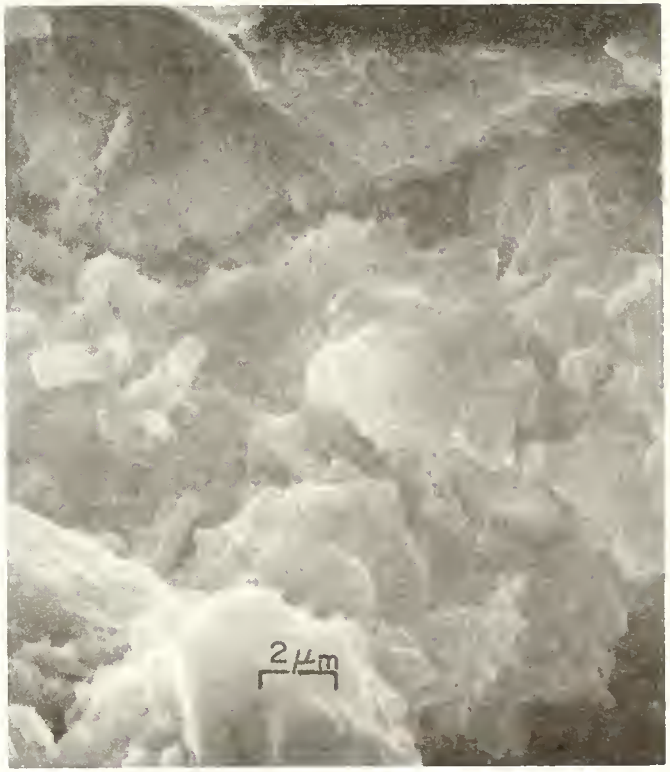

Figure 26. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at 36 Hours. (x 5000).

Figure 27. SEM Micrograph. Low Porosity Cement Paste, W:C 0.22, at 2 Days. (x 1000).

Figure 28. SEM Micrograph. Microstructure of Low Porosity Cement Paste, W:C 0.24, at 7 Days. (x 2000).

Comparatively little additional hydration takes place after 2 days according to the results of Figure 10, and this is reflected by the microstructure, which does not change very much. The structure is virtually featureless at 7 days, as indicated in Figure 28 taken at a low magnification and Figures 29 and 30 at higher magnification. There is a little pore space left, however, as shown in Figure 29.

Examination of the pastes at 28 days indicated further progress toward a completely massive microstructure. A low magnification view is given in Figure 31. One unusual feature is observed at higher magnifications at this stage; the presence of very small, "dot-like" protuberances on the fracture surfaces of otherwise smooth and featureless areas of massive hydration products. These are clearly indicated in Figures 32 - 34.

Even at this stage formation of the massive structure is not quite complete. On diligent search it is possible to find a few areas like that shown in the center of Figure 35, where residual void space views in a local region. Furthermore, as indicated in Figure 36 at higher magnification, individual hydration particles have been retained in these unusual areas, and there are a number of small equidimensional grains that are probably Type III C-S-H gel; thin plates that are probably an AFm hydration product (perhaps $C_4A\bar{C}H_{11}$) and some elongated

Figure 29. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 7 Days. (a) (x 5000).

Figure 30. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 7 Days. (b) (x 5000).

Figure 31. SEM Micrograph. Microstructure of Low Porosity Cement Paste, W:C 0.24, at 28 Days. (x 1500).

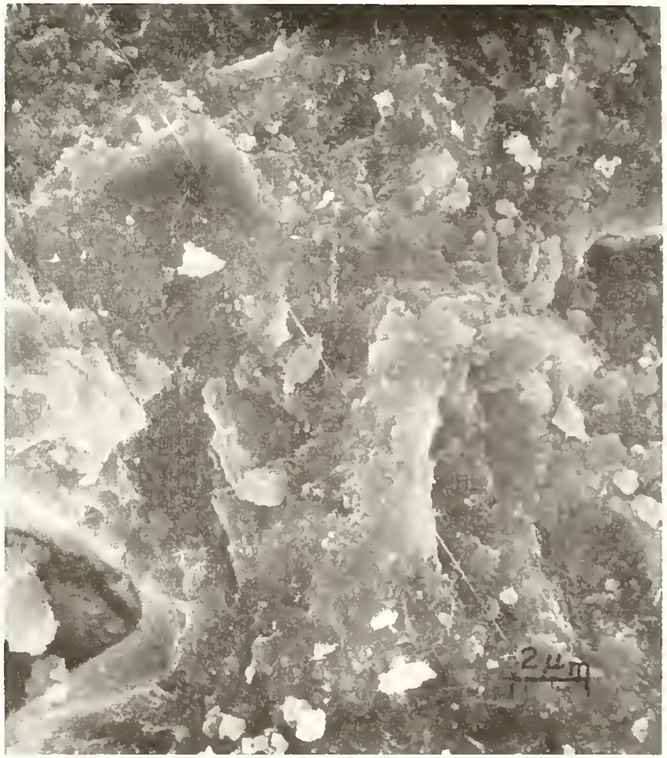

Figure 32. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 28 Days. (a) (x 5000).

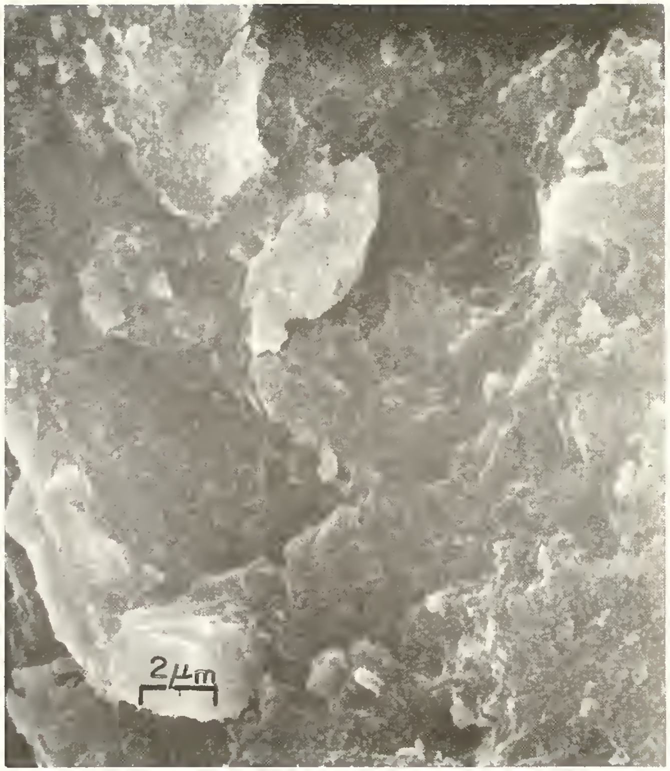

Figure 33. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 28 Days. (b) (x 5000).

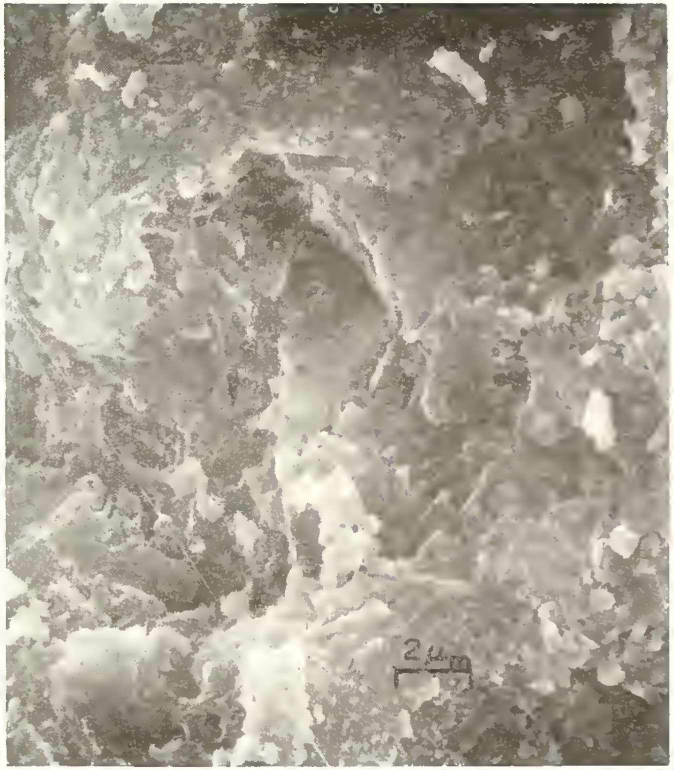

Figure 34. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 28 Days. (x 5000).

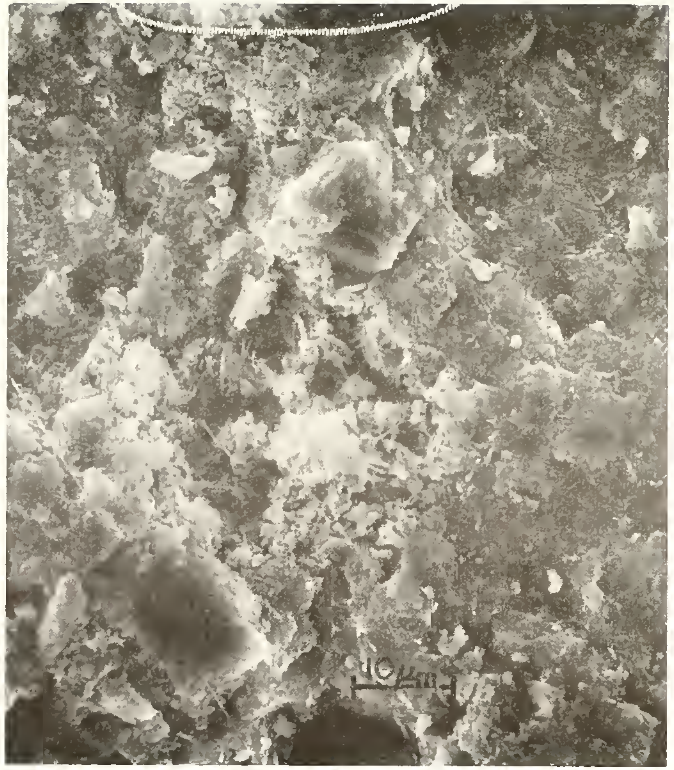

Figure 35. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 28 Days. (x 1500).

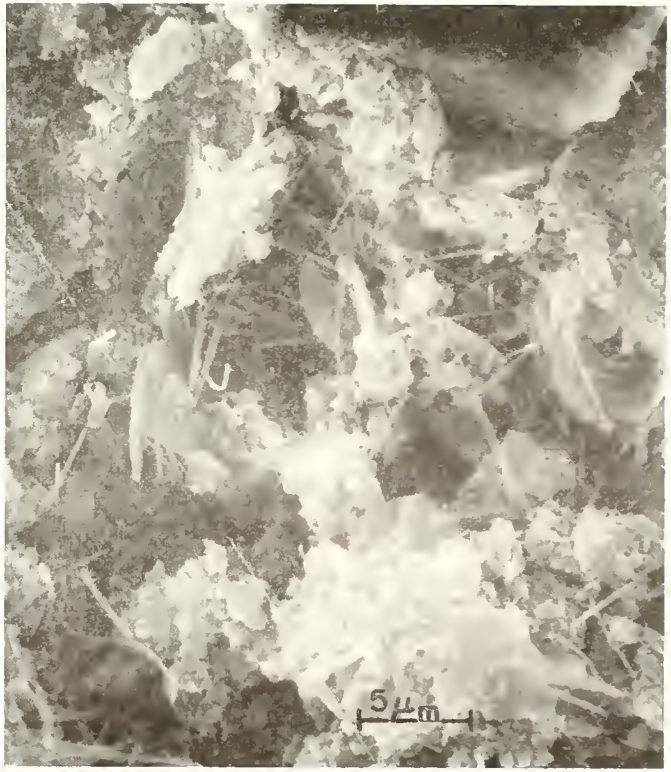

Figure 36. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 28 Days. Detail. (x 3000).

rod-shaped or needle-like particles that appear to be AFt hydration products, possibly $C_6A\bar{C}_3H_{30}$.

The coexistence of areas of this kind (few as they are) with the large preponderance of the massive areas of Figures 32 - 34 show clearly that cement paste is not necessarily homogeneous in different areas and that one must be careful in describing microstructural features to distinguish "typical" from "unusual" fields.

At 90 days, the microstructural features described at 28 days have persisted relatively unchanged. Typical low magnification views are shown in Figures 37 and 38, and the massive sturcture at higher magnification is shown in Figure 39. The very occasional areas of void space and individual particle morphology do persist even at 90 days, as indicated in a general view in Figure 40, and in a higher magnification view of a different area in Figure 41. Presumably a few such areas can persist indefinitely in the hardened paste.

Finally, an SEM examination was made of the bottle hydrated low porosity cement (W:C 10) described earlier in the section on ignition loss. This specimen was examined after 140 days of continuous rotation. The specimen formed a hardened mass that rotated in the water solution as a single rotating solid unit.

The structure is quite different from that of the low porosity paste prepared at low W:C ratio as previously

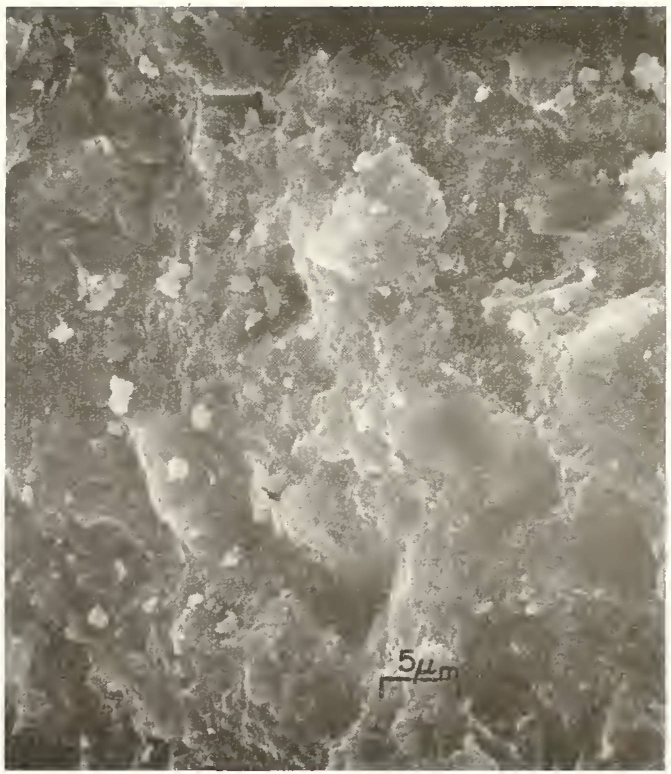

Figure 37. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 90 Days. (x 2000).

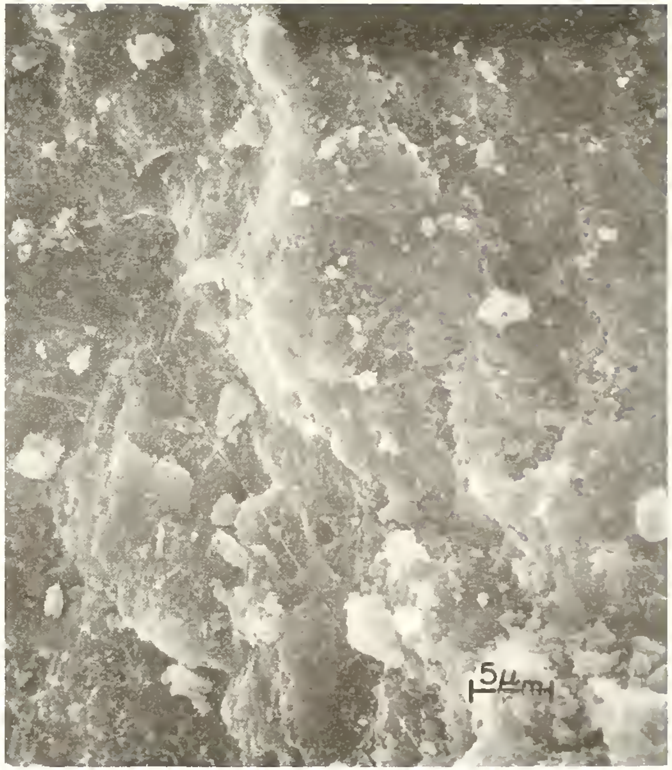

Figure 38. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 90 Days. (x 1700).

Figure 39. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 90 Days. (x 6000).

Figure 40. SEM Micrograph. Microstructure of Low Porosity Cement Paste, W:C 0.24, at 90 Days. (x 1500).

Figure 41. SEM Micrograph. Low Porosity Cement Paste, W:C 0.24, at 90 Days. (x 3500).

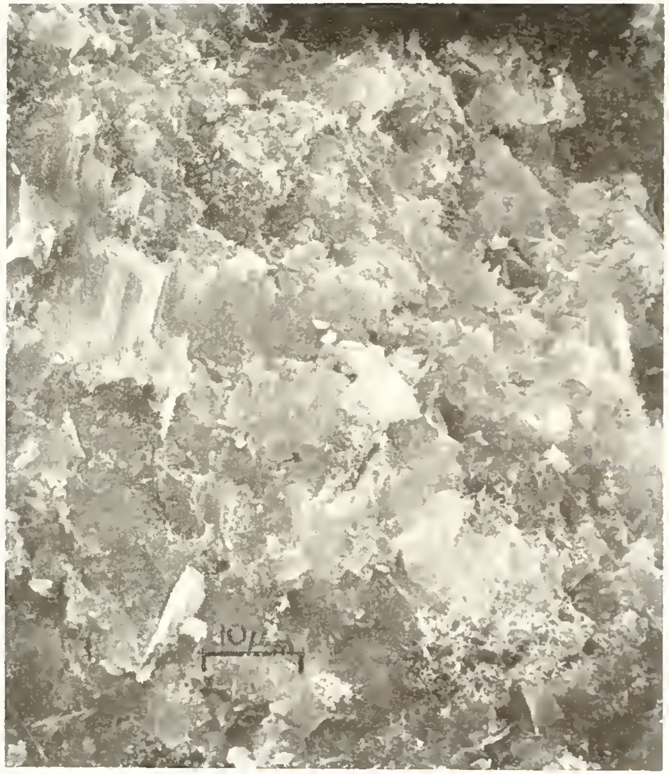

Figure 42. SEM Micrograph. Microstructure of Bottle Hydrated Low Porosity Cement Paste, W:C 10, at 140 Days. (x 1500).

described, and appears very much like that of conventional cement paste. An overall view at low magnification is shown in Figure 42. There are areas of reticular mesh structure (Type II hydration product) and some fibrous Type I product as indicated in Figure 43, and clearly defined stacks of massive calcium hydroxide crystals, as shown in Figure 44. The interlayering of the calcium hydroxide crystals with areas of C-S-H gel product (of Type III morphology is also clearly visible in Figure 44. Another area showing both features at different magnification is seen in Figure 45. The massive featureless zones typical of hydration product formed at low W:C ratio is not common in this material.

In summary, the microstructure developed in low porosity cement paste at low W:C levels rapidly becomes a massive continuously fused structure that does not permit distinguishing of individual hydration product particles except in a few atypical residual pore areas. For the same cement mixture bottle hydrated at high W:C ratio, the microstructure that develops is very similar to that of ordinary Portland cement paste.

Characterization of Hydration Products

The hydration products formed in the low porosity cement pastes previously discussed have been examined by differential thermal analysis (DTA) and by x-ray diffraction (XRD). The presentation of these examinations follow.

Figure 43. SEM Micrograph. Bottle Hydrated Low Porosity Cement Paste, W:C 10, at 140 Days. (x 5000).

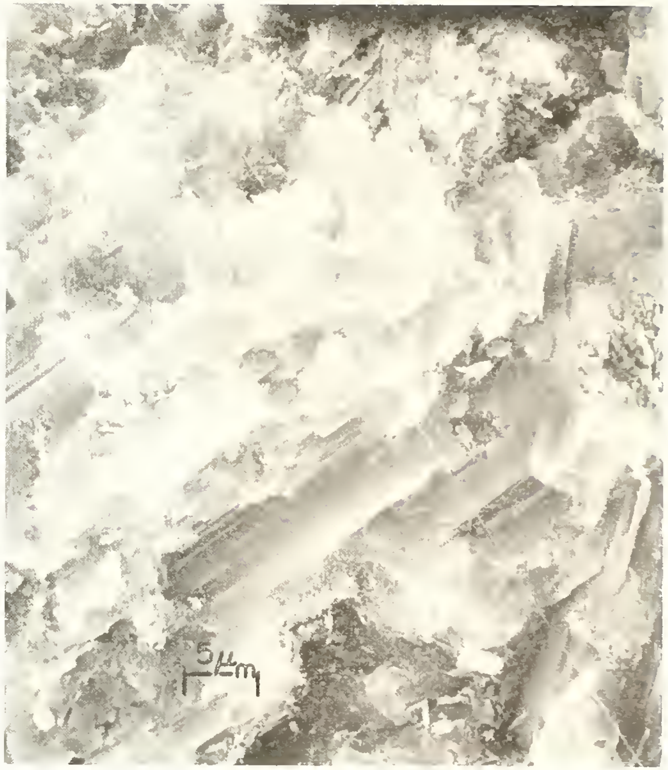

Figure 44. SEM Micrograph. Bottle Hydrated Low Porosity Cement Paste, W:C 10, at 140 Days. (x 2000).

Figure 45. SEM Micrograph. Bottle Hydrated Low Porosity Cement Paste, W:C 10, at 140 Days. (x 1000).

DTA Results. A series of DTA patterns representing stages of increased hydration are shown in Figure 46, and XRD patterns in Figure 47.

The DTA pattern for unhydrated low porosity cement represents that of the cement and the dry sodium bicarbonate and sulfonated lignin admixtures mixed in a SPEX mechanical mixer. The DTA patterns show several broad endothermic bulges between 100°C and 400°C, another broad endotherm bulge centering around 600°C, and a single sharp endothermic at 900°C, the latter presumably due to CO_2 evolution.

At the setting time (6 1/2 hours) the only apparent response is a reduction in the magnitude of all of the effects and a reduction in temperature for the strong CO_2 endotherm from 900°C to 870°C. No new features attributable to hydration product have developed, except a barely perceptible trace of an endotherm at 535°C, presumably due to $Ca(OH)_2$.

The magnitude of the high temeprature endotherm has increased slightly by 15 hours and what appears to be a lower temperature endothermic effect has developed at about 770°C preceding it. Again little or no $Ca(OH)_2$ seems to have been evolved.

By one day hydration products are clearly defined in terms of their DTA effects. There is a clear 200°C endotherm attributable to C-S-H gel and a significant

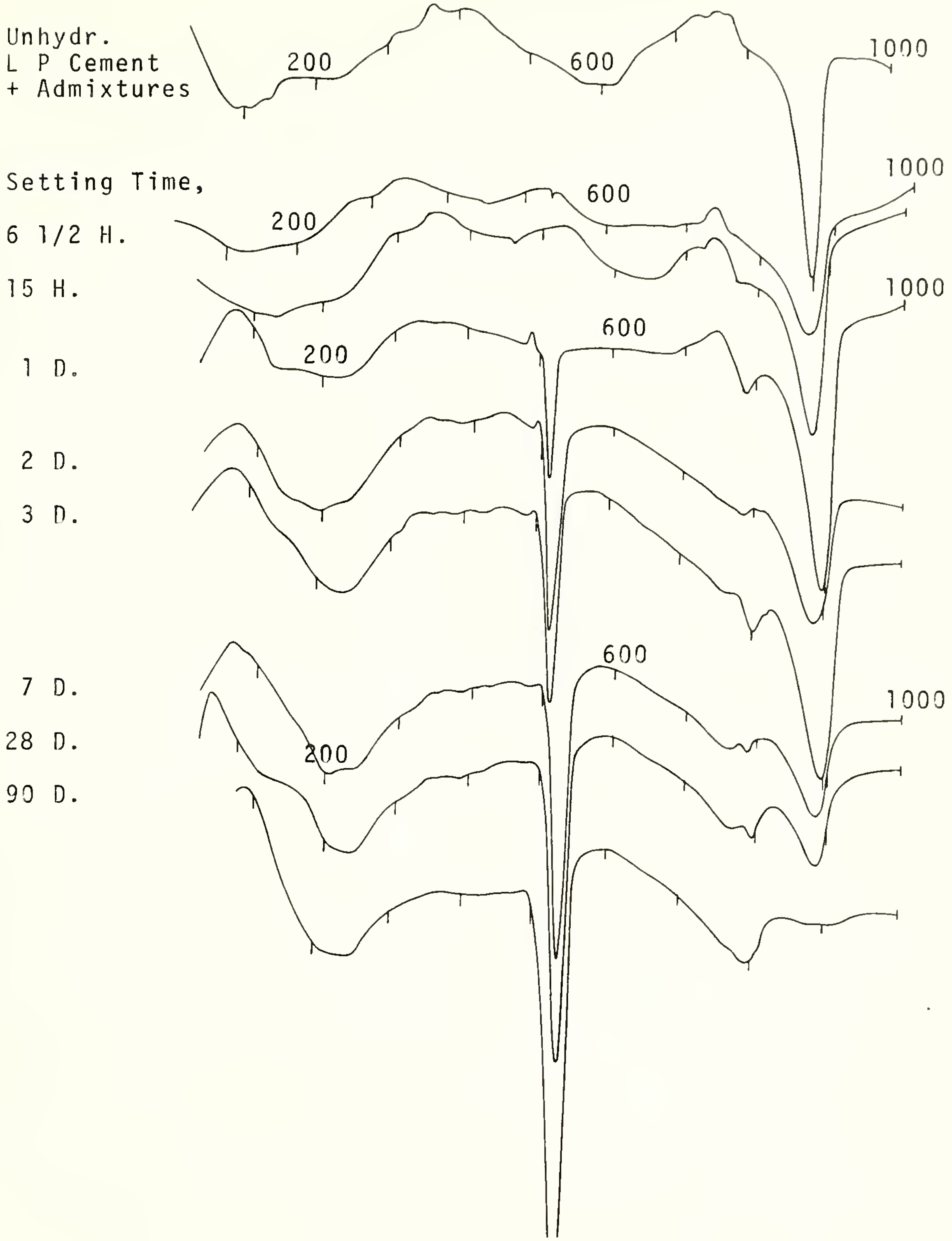

Figure 46. Differential Thermograms of Low Porosity Cement Paste, W:C 0.24, at Various Ages.

Figure 47. X-Ray Diffractograms of Unhydrated Ground Clinker Without Admixtures and of Low Porosity Cement Paste, W:C 0.24, at 28 Days.

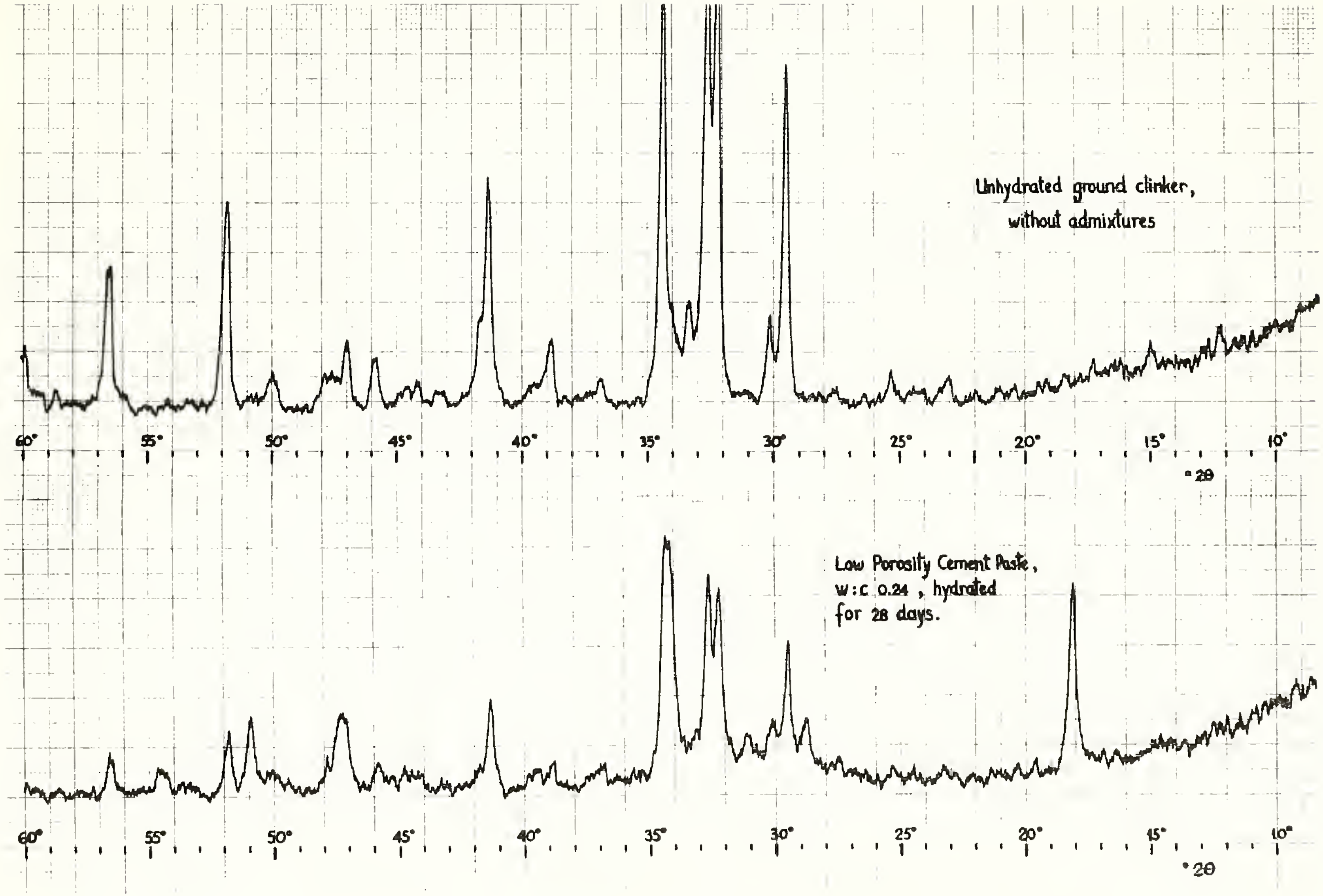
Unhydrated ground clinker,
without admixtures
60°
55°
50°
45°
40°
35°
30°
25°
20°
15°
10°
°2θ
Low Porosity Cement Paste,
w:c 0.24, hydrated
for 28 days.
60°
55°
50°
45°
40°
35°
30°
25°
20°
15°
10°
°2θ

Figure 47.

520°C endotherm attributable to $Ca(OH)_2$. Just before the 520°C endotherm is a small exotherm at 490°C, of unknown origin. Again there is a small endotherm at 790°C preceding the large endotherm at about 900°C. The magnitude of the latter has not changed very much.

At two days the C-S-H gel and the $Ca(OH)_2$ peaks are somewhat stronger. The small exotherm at 490°C has decreased slightly. The CO_2 evolution peak is somewhat weaker. The specimen at three days shows no significant changes, but marked changes occur by seven days. The $Ca(OH)_2$ peak is definitely larger, the CO_2 evolution peak definitely smaller, the endotherm at around 770°C has split into two small endothermic features at 760°C and 790°C respectively, and the small exotherm at 490°C has disappeared. By 90 days the double endotherm at 760°C and 790°C endotherms have apparently fused and formed a single large endotherm at 790°C, and the 900°C peak has almost disappeared. The $Ca(OH)_2$ endotherm at 540°C has further increased in size.

X-Ray Diffraction Results. X-ray diffraction patterns of randomly oriented powder mounts were run from powdered low porosity cement pastes hydrated as previously described and dried at 105°C; the x-ray patterns corresponding to the ground clinker without admixtures and to the 28 day paste are shown in Figure 47.

At setting time (6 1/2 hours), while the intensity of the peaks for the cement compounds appear to have been reduced, the x-ray pattern showed no detectable $Ca(OH)_2$, C-S-H compounds, or carbonate-bearing phases.

However, by one day the presence of crystalline $Ca(OH)_2$ was clearly indicated by peaks at 18.1°C and 34.1 2Θ. The C-S-H gel was undetectable and no crystalline carbonate-bearing compounds could be detected.

At 3 days the peaks for the cement compounds were significantly reduced to a further extent, and the main C_3A peak at 33.3 2Θ was almost gone. The crystalline $Ca(OH)_2$ content did not seem any greater than at 1 day.

At 28 days the x-ray diffraction pattern was basically unchanged from that developed at 3 days.

Basically, the x-ray diffraction results indicated that $Ca(OH)_2$ is the only crystalline hydration product detectable.

Interpretation of the Pattern of Hydration of Low Porosity Cement

The sequence of changes in the microstructural appearance, DTA pattern, and XRD patterns described previously can be restated and interpreted as follows:

At the earliest stages of hydration (1 to 2 hours) no obvious development of AFt hydration products, such as formed in ordinary gypsum bearing cement pastes, was detected; in fact there was little apparent change in the appearance of the paste from that of the clinker.

At the setting time (6 1/2 hours) again little visible change in the microstructural appearance can be detected, but a trace of $Ca(OH)_2$ has been detected in DTA and some evidence for C-S-H gel development can be inferred from the DTA endotherm in the 100°C - 300°C region. DTA also shows a strong peak presumable due to carbon dioxide evolution at 900°C, and a much smaller one at 770°C. The former peak was present in the DTA pattern of the original dry mixture of ground clinker and the admixtures, but the latter was not.

By 15 hours, the SEM results indicate that much hydration has taken place, and coatings of thin plate hydration products surround the residual grains of ground clinker, and clusters of them are visible in the pores. Hydration products in the form of thin plates (AFm phase?) appear for the first time.

By 24 hours, SEM reveals much greater concentrations of hydration products and they are more closely packed; particles that are tentatively identified as C-S-H gel of Type III are prominent, and a few elongated particles are present. Much of the hydration product seems massive and even-textured. Apparent embedded crystals of $Ca(OH)_2$ are detectable for the first time.

The $Ca(OH)_2$ is also readily detected by XRD and by a strong DTA peak at 520°C. DTA also indicates the increased content of C-S-H gel hydration products with an enlarged endotherm centered near 200°C. Other features opened in DTA include, for the first time, a small exotherm at 490°C of unknown significance.

By 2 days, SEM indicates that almost all of the hydration products have "fused" into a mass with individual particles mostly not separatable. DTA results show stronger endotherms for C-S-H gel and for $Ca(OH)_2$, and the 490°C exotherm is slightly weaker. Subsequent changes in morphology are minor. Some little pore space is retained indefinitely, and a few individual particles of hydration products continue to be detectable in these few atypical areas.

XRD results showed a progressive decrease in the peak heights for the cement minerals, and the main C_3A peak at 33.3 2Θ was essentially gone by 3 days. The $Ca(OH)_2$ peaks progressively increased. No clear objective indication of C-S-H gel could be made at any stage.

The DTA results show some changes over time. By 7 days the small 490°C exotherm had disappeared and the 790°C endotherm had split into 2 separate peaks and increased in magnitude; however, these two peaks eventually fused to a single enlarged peak at 790°C (by 90 days). The original CO_2 evolution peak at 900°C had decreased significantly in magnitude by 28 days and almost disappeared by 90 days. C-S-H gel and especially

$Ca(OH)_2$ peaks increased progressively. These results indicate that hydration of ground clinker in the low porosity system gives rise to the same basic hydration products, C-S-H gel and crystalline $Ca(OH)_2$, that hydration of gypsum-bearing cement produces, but there are some differences in (a) microstructure, which becomes massive at an early stage and which never develops significant quantities of Type I or Type II C-S-H gel, (b) in that no ettringite is formed and very few elongated particles develop, and (c) in DTA effects that are peculiar to this system.

The low porosity paste hydrated at W:C ratio of 10 in a rotating container appeared to develop a more nearly "conventional" microstructure such as one would associate with ordinary cement paste, suggesting that at least some of the differences noted above may be due to the effect of the low W:C ratio used, rather than the effect of the chemistry of the admixtures that replace the gypsum.

Pore Size Distribution

As a part of the study of the microstructure of low porosity cement paste, investigations were made on a paste having water to cement ratio 0.24 to determine its pore size distribution with the progress of the hydration process. High pressure mercury intrusion up to 410 MPa (60,000 psi), was carried out on specimens that were oven-dried prior to the determinations. The results are plotted in Figure 48 and important features are summarized in Table 7. The total intrusion at the end of each test represents that pore volume in the paste having interconnected pores whose minimum pore diameter is about 21 Å. The diameter of the intruded pores was calculated from the Washburn equation

$$P = \frac{-4\ \gamma \cos \Theta}{d} ,$$

where:

P = pressure required to intrude a pore,

d = diameter of the intruded pore,

γ = surface energy of the liquid,

Θ = contact angle between the liquid and the pore wall.

From the study by Winslow and Diamond (27) the values $\Theta = 117°$ and $\gamma = 484$ dynes/cm were adopted for the present work. From Table 7 it may be seen that the intruded volume decreases progressively as the cement paste ages and that the threshold diameter of intrusion in the paste does not change after the first day.

In Figure 48 it can be seen that after the threshold diameter is reached the slope of the intrusion vs. log diameter plot is steep to diameters just smaller than 100 Å and then becomes less steep. The curves shift to the left with increasing age, that is, the pores become increasingly finer with age.

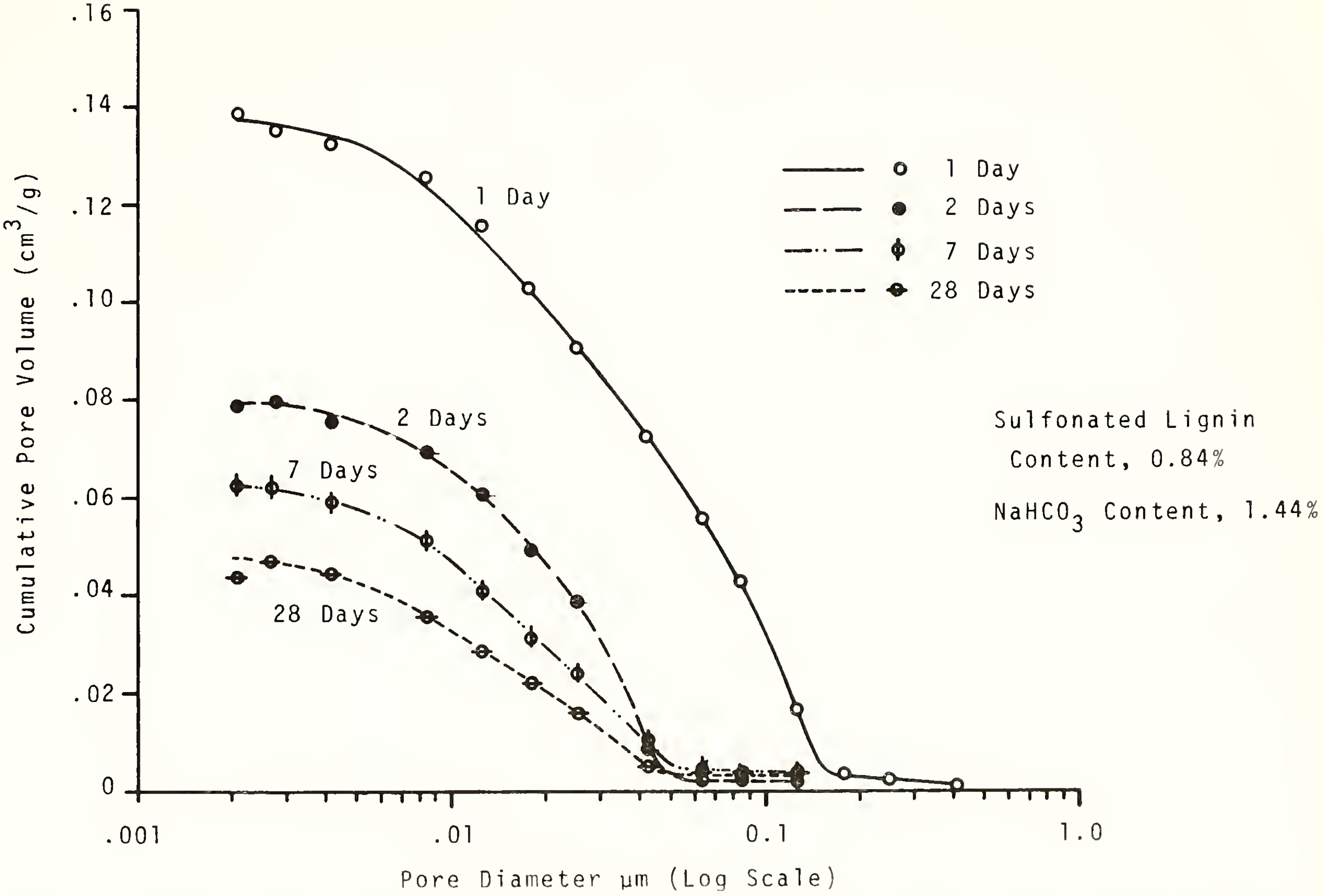

Figure 48. Pore Size Distribution Curves of Low Porosity Cement Paste, W:C 0.24, at Various Ages.

Table 7. Intruded Volume and Threshold Diameter of Low Porosity Cement Paste.*

Age, Days	Estimated Degree of Hydration, %	Intruded Volume cm^3/g	Threshold Diameter Å
1	24	.139	1800
2	50	.079	600
7	59	.062	600
28	62	.047	600

* Sulfonated lignin content. 0.84%; $NaHCO_3$ content, 1.44%.

Comparing the results of the present work to those reported by Winslow and Diamond (27), which correspond to conventional cement paste having W:C 0.40, the following can be said:

a) The threshold diameter of the low porosity cement paste is smaller at all ages; suggesting that this paste is "tighter" at any given age.

b) The total intrusion in low porosity cement paste is smaller at all ages, indicating that this paste is less porous.

c) The pore size distribution curve of low porosity cement paste as plotted on a logarithmic diameter scale shows similar shape evolution with time.

Permeability

Concrete structures should withstand the structural and environmental conditions for which they were designed, without suffering deterioration during their useful lives. Permeability of concrete is one of the factors that almost always plays an important role in deterioration problems such as frost damage, corrosion of steel, and alkali-aggregate reaction.

The permeability of concrete is probably strongly influenced by the permeability of its cement paste component. The permeability of low porosity cement paste (kept always wet) was measured along with that of similar specimens of conventional cement paste by Mr. Kozo Mizutani, a Purdue Univeristy graduate student. Details on the prepatation of the specimens were given in page 29. A summary of the results obtained is presented in Table 8. The values in the table correspond to average values of a number of repeated measurements. The table indicates that low porosity cement paste is much less permeable than conventional cement paste at all ages and for all W:C ratios by a factor of the order of magnitude of 10. The coefficient of permeability (K) of mature low porosity cement paste is about 4.0×10^{-11} mm/sec. These results suggest that the permeability of low porosity concrete might be considerably less than that of a similar conventional concrete and, hence, that low porosity concrete should be more durable.

Compressive Strength of Low Porosity Cement Paste

The ultimate purpose of cement paste is to provide adequate strength to the concrete to be made with it. The next sections will cover the strength tests carried out in this work to investigate low porosity cement.

Low porosity cement paste was tested to failure in compression, using cube specimens 50.8 mm (2 in.) on a side.

The development of strength with time is tabulated in Table 9, and plotted in Figures 49 and 50. Most of the values in the table represent means of three or more

Table 8. Coefficient of Permeability of Low Porosity Cement Paste.

	W:C Ratio	Measured Permeability, mm/sec (in./sec), at time indicated	
		One Month	Seven Months
Low Porosity Cement Paste	.22	14×10^{-11} $(.55 \times 10^{-11})$	6×10^{-11} $(.24 \times 10^{-11})$
	.30	9×10^{-11} $(.35 \times 10^{-11})$	4×10^{-11} $(.16 \times 10^{-11})$
	.35	4×10^{-11} $(.16 \times 10^{-11})$	4×10^{-11} $(.16 \times 10^{-11})$
Conventional (Portland) Cement Paste	.35	17×10^{-10} $(.67 \times 10^{-10})$	20×10^{-10} $(.79 \times 10^{-10})$
	.40	12×10^{-10} $(.47 \times 10^{-10})$	5×10^{-10} $(.20 \times 10^{-10})$
	.50	17×10^{-10} $(.67 \times 10^{-10})$	5×10^{-10} $(.20 \times 10^{-10})$

Table 9. Compressive Strength of Low Porosity Cement Paste.*

W:C	Compressive Strength, MPa (psi), at								
Ratio	15 Hrs	18 Hrs	21 Hrs	1 Day	2 Days	3 Days	7 Days	28 Days	90 Days
0.22	14.8	43.8	45.9	65.5	82.1	94.1	100.7	113.1	132.0
	(2150)	(6350)	(6650)	(9500)	(11900)	(13650)	(14600)	(16400)	(19150)
0.23	10.0	23.8	49.0	66.2	74.8	88.3	97.6	116.6	110.3
	(1450)	(3450)	(7100)	(9600)	(10850)	(12800)	(14150)	(16900)	(16000)
0.24	1.7	2.8	6.9	41.0	75.5	90.7	101.7	121.0	117.6
	(250)	(400)	(1000)	(5950)	(10950)	(13150)	(14750)	(17550)	(17050)

*Sulfonated lignin content, 0.84%; $NaHCO_3$ content, 1.44%.

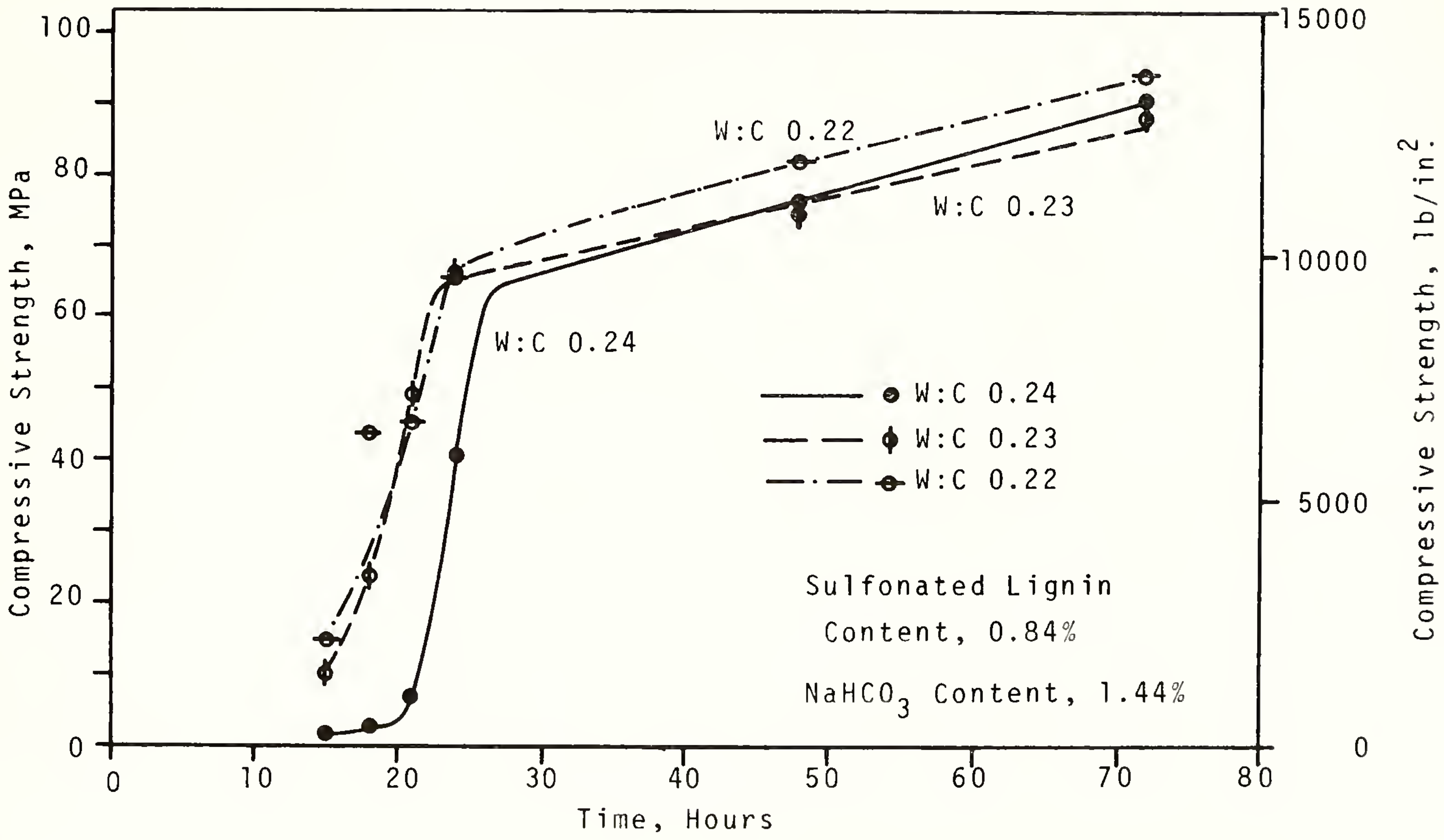

Figure 49. Compressive Strength of Low Porosity Cement Paste. Early Stages.

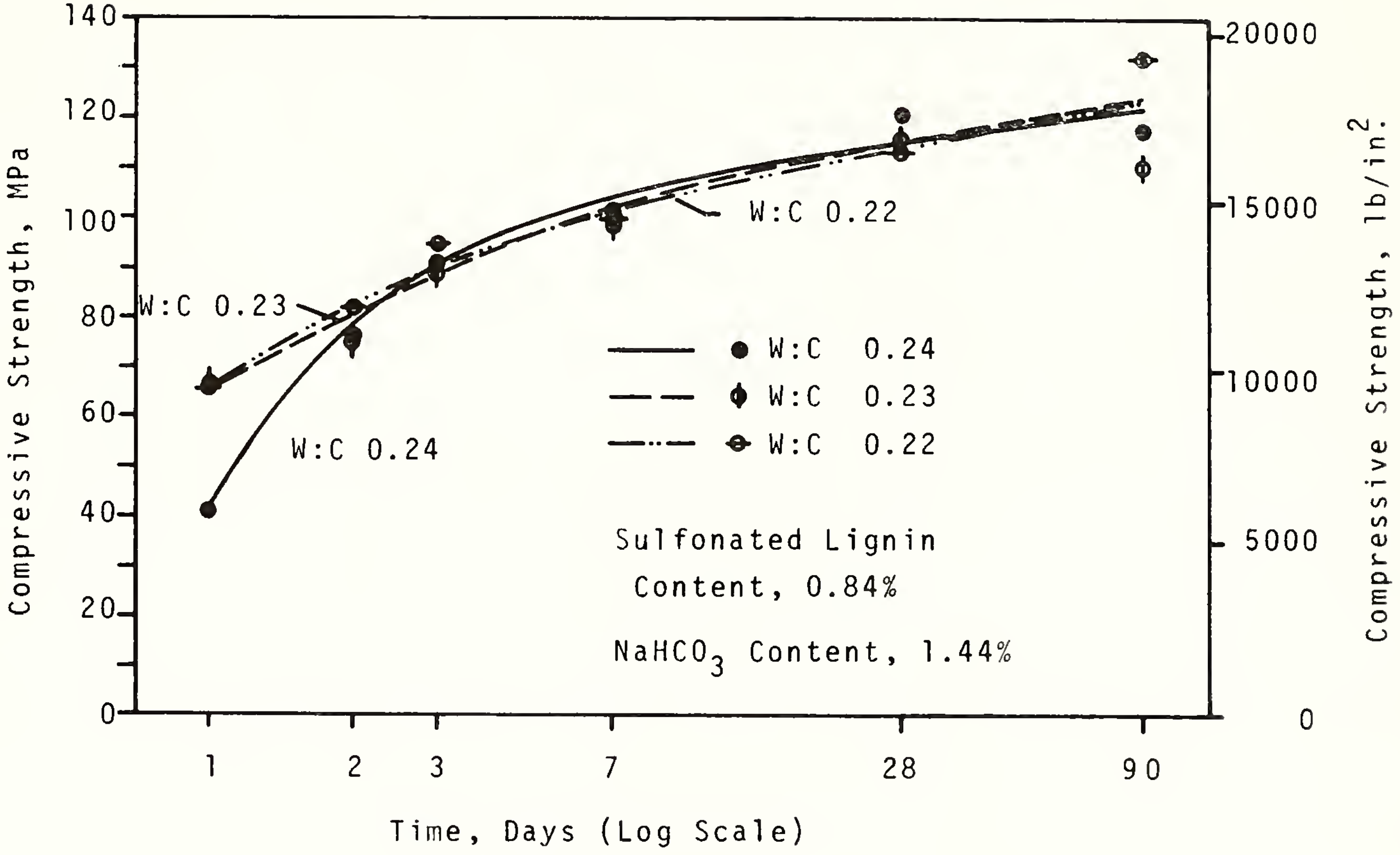

Figure 50. Compressive Strength of Low Porosity Cement Paste.

compressive strength series, each composed of three tested cubes. In Figure 49 it may be seen that the compressive strength at early ages, say up to 24 hours, is significantly lower in the W:C 0.24 pastes; however, at two and three days there is only a slight difference in compressive strength between the W:C 0.22, 0.23 and 0.24 pastes. Low porosity cement pastes having W:C 0.22 or W:C 0.23 after only one day of hydration reach compressive strengths of about 66 MPa (9,500 psi). Yudenfreund et al. (28), obtained compressive strengths at one day of the order of 97 MPa (14,000 psi) on 25.4 mm (1.0 in.) low porosity cement paste cubes. Because of size effects (16), it is difficult to compare the results of Yudenfreund et al. directly with the present data. The results at later ages shown in Figure 50 indicate that compressive strengths are not very different between the pastes of W:C 0.22, 0.23 and 0.24, although the W:C 0.22 paste shows slightly higher compressive strength values at all ages except 28 days. Compressive strength values of the paste at 2 days and at 28 days are about 76 MPa (11,000 psi) and 117 MPa (17,000 psi), respectively, which suggests that low porosity cement paste can probably make high-strength concrete even at early ages.

Compressive Strength of Low Porosity Concrete

The low porosity concretes for which compressive strengths were measured were prepared as indicated on page 32. The mix design and the methods of mixing were developed after a process of trial and error, to provide appropriate workability and handling properties in view of the unusual characteristics of the low porosity cement material. The design and methods are not necessarily the best that can be developed for the use of low porosity cement in concrete, and merely represent a system that works in practice.

The compressive strengths for low porosity concrete made at W:C ratios of 0.26 to 0.32 were measured at ages ranging from 1 day to 28 days, with a few also measured at 90 days.

The compressive strengths of these low porosity concretes are tabulated in Table 10, and plotted in Figures 51, 52 and 53. Most of the values in the table represent mean values of three tested cylinders, except those for mixes 1, 2 and 3, which represent mean values of three series each composed of three tested cylinders, i.e., nine values in all. All concrete mixes had cement factor of 8.0 bags per cu yd (450 Kg/m^3) and aggregate to cement ratio between 4.0 and 4.3 except concrete mix No. 13 which had a cement factor of 10.0 bags per cu yd (560 Kg/m^3) and an aggregate cement ratio of 3.0.

Comparing concrete mixes 1, 2, 3 and 4 which vary only in W:C ratio, it can be said that the lower the W:C ratio the higher the compressive strength at any age.

Table 10. Influence of Some Variables on the Compressive Strength of Low Porosity Concrete.

Mix	W:C Ratio	Sulf. Lignin Content, %*	$NaHCO_3$ Content, %*	Compressive Strength, MPa (psi)					
				1 Day	2 Days	3 Days	7 Days	28 Days	90 Days
1	0.26	0.84	1.44	2.1 (300)	45.9 (6650)	56.2 (8150)	64.8 (9400)	70.7 (10250)	76.2 (11050)
2	0.28	0.84	1.44	2.1 (300)	39.3 (5700)	53.1 (7700)	62.4 (9050)	67.6 (9800)	77.6 (11250)
3	0.30	0.84	1.44	1.7 (250)	37.9 (5500)	47.6 (6900)	58.3 (8450)	63.4 (9200)	73.4 (10650)
4	0.32	0.84	1.44	0.7 (100)	12.1 (1750)	30.0 (4350)	38.3 (5550)	49.0 (7100)	
5	0.28	0.57	1.44	---	49.0 (7100)	58.6 (8500)	66.6 (9650)	72.8 (10550)	
6	0.28	0.66	1.44	1.0 (150)	37.2 (5400)	59.0 (8550)	63.4 (9200)	72.4 (10500)	
7	0.28	0.75	1.44	2.1 (300)	46.6 (6750)	55.5 (8050)	62.4 (9050)	70.7 (10250)	
8	0.28	0.93	1.44	2.1 (300)	46.6 (6750)	55.9 (8100)	63.4 (9200)	71.7 (10400)	
9	0.28	0.70	0.80	0.7 (100)	1.4 (200)	24.8 (3600)	62.8 (9100)	79.3 (11500)	
10	0.28	0.70	1.00	0.3 (50)	20.0 (2900)	49.7 (7200)	69.7 (10100)	80.0 (11600)	
11	0.28	0.70	1.40	5.5 (800)	51.0 (7400)	60.3 (8750)	62.8 (9100)	81.7 (11850	
12	0.28	0.70	1.60	3.8 (550)	40.7 (5900)	53.8 (7800)	62.8 (9100)	73.1 (10600)	
13	0.28	0.70	1.20	1.4 (200)	49.0 (7100)	61.0 (8850)	69.0 (10000)	73.1 (10600)	

* By weight of cement.

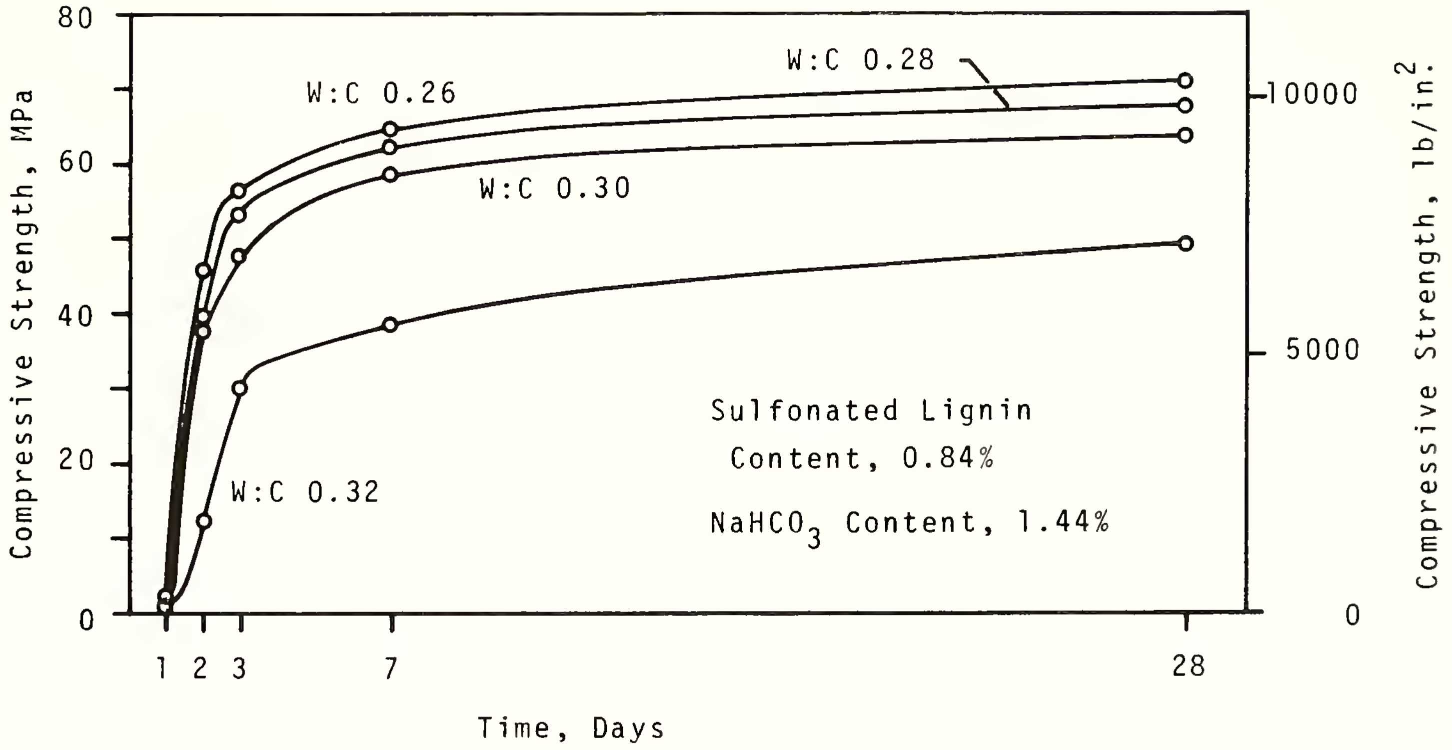

Figure 51. Effect of W:C Ratio on the Compressive Strength of Low Porosity Concrete.

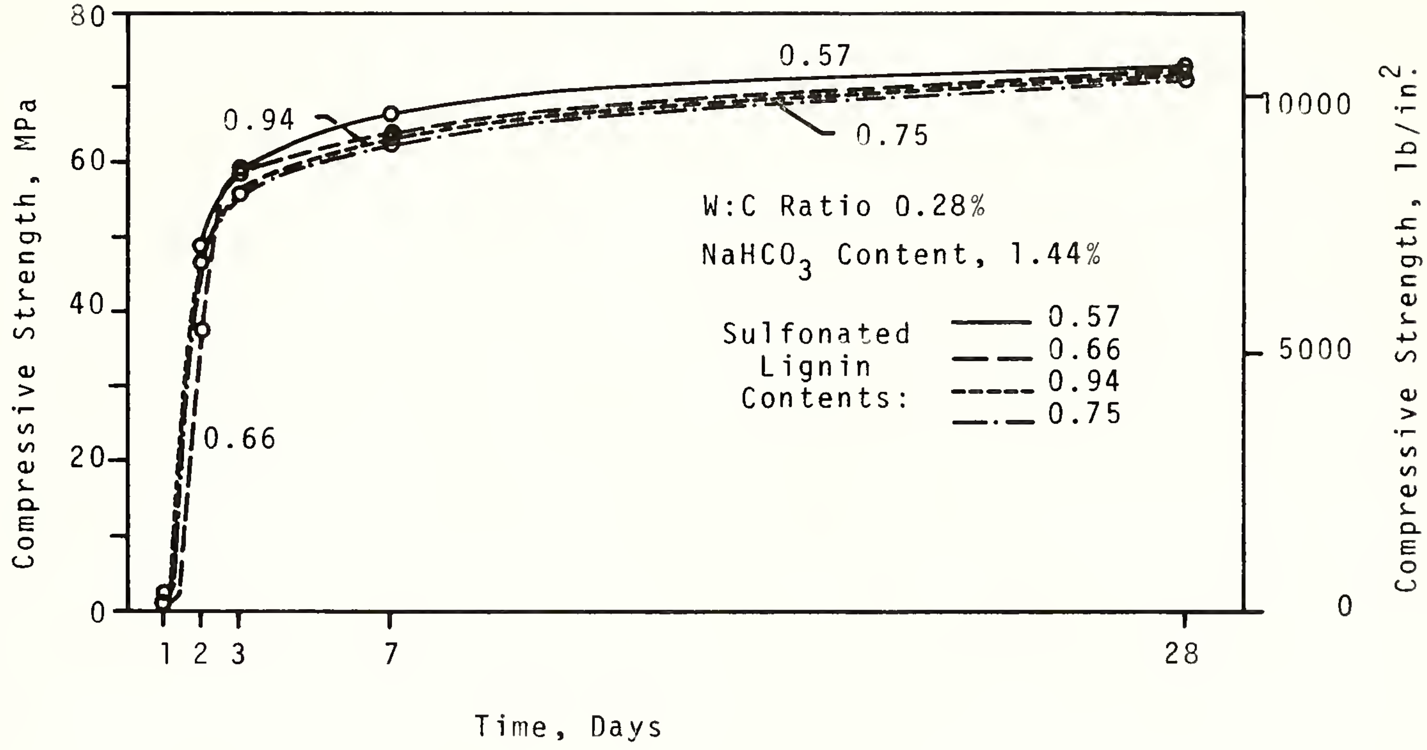

Figure 52. Effect of Sulfonated Lignin Content on the Compressive Strength of Low Porosity Concrete.

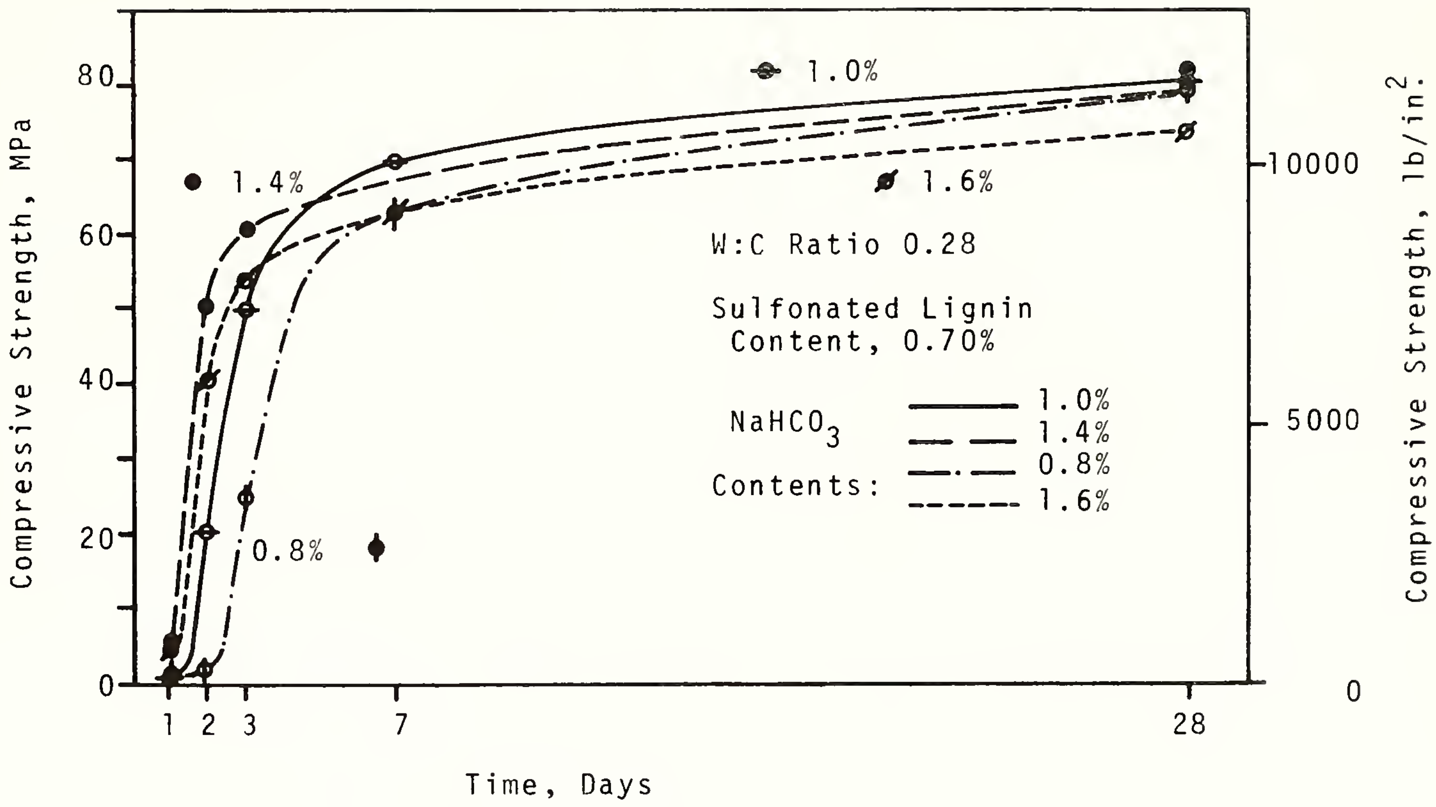

Figure 53. Effect of Sodium Bicarbonate Content on the Compressive Strength of Low Porosity Concrete.

The effect is small for variations from W:C 0.26 to W:C 0.30, but increasing the value to W:C 0.32 causes a relatively large effect. Compressive strength values of low porosity concrete having W:C 0.26 are 46 MPa (6,650 psi) at two days and 71 MPa (10,250 psi) at 28 days. For the W:C 0.30 concrete the corresponding values are 38 MPa (5,500 psi) at 2 days and 63 MPa (9,200 psi) at 28 days. The W:C 0.28 concrete shows compressive strength values in between those of the W:C 0.26 and the W:C 0.30 concretes. By 90 days these three low porosity concretes have about the same compressive strength value, 76 MPa (11,000 psi).

The effect of variation of sulfonated lignin content on the compressive strength of low porosity concrete can be seen by comparing concrete mixes 5, 6, 7 and 8 (see Table 10 and Figure 52). As far as compressive strength is concerned, there is practically no difference between concretes having different sulfonated lignin contents, i.e., concrete strength is insensitive to variation in this factor. Compressive strength values observed in these mixes are about 46 MPa (6,600 psi) at 2 days and 72 MPa (10,400 psi) at 28 days.

The influence of the $NaHCO_3$ content is indicated by comparing the results for concrete mixes 9, 10, 11 and 12. In these mixes the sulfonated lignin content was kept constant at 0.70% of the weight of the cement, this value being chosen after observations of the workability of concrete at various sulfonated lignin contents. At early ages (up to three days), the compressive strength of concrete is significantly influenced by its $NaHCO_3$ content; from seven days on, however, the strength response seems to be independent of the $NaHCO_3$ content in the concrete. Variations in contents ranging from 1.0 to 1.6 percent produced no significant strength variations, but reducing the $NaHCO_3$ content to 0.8% caused some delay in strength gain, reflected in lower strengths at 2 and 3 days. Typical compressive strength values of these concretes are about 63 MPa (9,100 psi) at 7 days and 79 MPa (11,500 psi) at 28 days. These values are slightly higher than the corresponding values of concrete mix No. 2 which had a sulfonated lignin content of 0.84% (instead of 0.70%). The highest early and final compressive strength results were attained when the $NaHCO_3$ content was 1.4%.

The influence of the cement content in low porosity concrete was investigated only briefly. Concretes were made having cement factors of 7.0, 8.0 and 10.0 bags per cu yd (390, 450 and 560 Kg/m^3) and no specimens were cast for testing. The effect of the cement content might be indicated by comparing concrete mixes 2 and 13 (cement factor 8.0 and 10.0 bags per cu yd (450 and 560 Kg/m^3, respectively); however, it should be mentioned that there is a slight difference in the admixture concentration between them. The compressive strength of the richer mix is slightly higher at all ages except at one day. In the present work the compressive strength of low porosity concrete having W:C ratio 0.26 (and $NaHCO_3$ content of 1.44% and sulfonated lignin content of 0.84%) is 65 MPa (9,400 psi) at 7 days, and 71 MPa (10,250 psi) at 28 days. Skalny et al. (23), for steam-cured concrete specimens of low porosity concrete having W:C 0.26, obtained approximately 83 MPa (12,000 psi) at 7 days, and 96 MPa (14,000 psi) at 28 days. Hattori and Yamakawa (11), for specimens of Portland cement concrete having a super water-reducer made at W:C 0.27 obtained approximately 77 MPa (11,200 psi) and 7 days, and 87 MPa (12,600 psi) at 28 days.

Flexural Strength of Low Porosity Concrete

The tensile or flexural strengths of concrete have been found to be critical in the behavior of concrete members subjected to flexural loading in road slabs and airfield runways. Flexural strength (modulus of rupture) was investigated for concrete made with low porosity cement. Table 11 presents the results obtained along with some additional information. It may be said that the flexural strength of low porosity concrete is not affected by its W:C ratio within the limited range investigated (W:C 0.26 to W:C 0.30). Flexural strengths at 28 days were about 8.4 MPa (1,220 psi), which is about

Table 11. Flexural Strength of Low Porosity Concrete.*

Concrete Mix	W:C Ratio	Age, Days	Compressive Strength MPa (psi)	Flexural Strength, MPa (psi)	$\frac{\text{Flexural Strength}}{\text{Compressive Strength}} \times 100$
1	0.26	28	70.6 (10250)	8.4 (1220)	11.9
2	0.28	28	67.7 (9800)	8.4 (1220)	12.5
3	0.30	28	63.3 (9200)	8.7 (1260)	13.7

* Sulfonated lignin content, 0.84% Wc; $NaHCO_3$ content, 1.44% Wc.

12% of the corresponding compressive strengths and significantly higher than is usual for conventional high strength concrete (19). The flexural strength: compressive strength ratio is slightly higher for the higher W:C ratios tested.

Dynamic Modulus of Elasticity of Low Porosity Concrete

Concrete structures under working conditions exhibit deformations which may be predictable to a certain extent. The stress-strain relationship of concrete in terms of its static Young's modulus of elasticity is difficult to measure properly since concrete is not quite linearly elastic. Often the stress-strain characteristics are measured dynamically, through measurement of pulse velocity, and expressed as a dynamic modulus of elasticity. The dynamic modulus corresponds approximately to the initial tangent modulus of the stress-strain curve of concrete (16).

Investigation of the dynamic modulus of elasticity of low porosity concrete was carried out on test beams made of concrete having W:C 0.26, W:C 0.28 and W:C 0.30. Table 12 shows the results obtained. The values were calculated as detailed in page 35. It may be seen that the dynamic modulus of elasticity of the concrete slightly decreases with increasing W:C ratio. The values obtained for low porosity concrete are of the

Table 12. Dynamic Modulus of Elasticity of Low Porosity Concrete.*

Concrete Mix	W:C Ratio	Age, Days	Compressive Strength, MPa (psi)	Dynamic Modulus of Elasticity, MPa (psi)
1	0.26	28	70.7 (10250)	59800 (8.67×10^6)
2	0.28	28	67.6 (9800)	59500 (8.62×10^6)
3	0.30	28	63.4 (9200)	58000 (8.42×10^6)

* Sulfonated lignin content, 0.84% Wc;

$NaHCO_3$ content, 1.44% Wc.

order of 59,000 MPa (8.6 x 10^6 psi) at 28 days.

Conventional high-strength concretes having a 28 day compressive strength similar to that of these low porosity concretes have a dynamic modulus of elasticity of about 45,000 MPa (6.5 x 10^6 psi) (19), which is considerably lower than the low porosity concrete results recorded here.

CHAPTER V

SUMMARY

A series of examinations were carried out on the behavior and technical characteristics of cement pastes and of concretes made using "low-porosity" cement, a finely-ground, gypsum-free Type I clinker regulated with admixture of specially-developed sulfonated lignin and sodium bicarbonate.

The consistency and flow behavior of fresh pastes made at W:C ratios of 0.22, 0.23 and 0.24 were examined. Pastes prepared at the two higher water contents were found to be sufficiently fluid to be readily pourable, and to exhibit little or no bleeding. Pastes prepared at W:C 0.22 were pourable only with difficulty, some vibration being required to assist in maintaining fluidity.

Concretes made at W:C ratios between 0.26 and 0.32 were examined for workability and flow properties in the fresh state. The influence of the contents of sulfonated lignin and of $NaHCO_3$ on these properties were investigated, and the influence of the cement content touched at briefly.

It was seen that W:C 0.30 concretes have excellent workability being freely displaceable, self-compacting, and not segregating or bleeding, that workable concrete of slightly less fluidity was produced using W:C 0.28, but that further reduction in the W:C ratio did not produce freely-flowing and easily workable concrete, at least with the aggregates and mix design used.

Sulfonated lignin contents of 0.66% of the weight of the cement or greater produced concretes of satisfactory workability at W:C 0.28.

Variations in $NaHCO_3$ content of 0.8% and 1.0% of the weight of the cement produced concretes of good workability at W:C 0.28, but increased $NaHCO_3$ contents interfered somewhat with desireable flow characteristics.

Observations on the behavior of relatively lean low porosity concrete trial mixes having cement factor 7.0 bags per cu yd (390 Kg/m^3) with W:C 0.28 indicated that such mixes did not flow satisfactorily under vibration in the usual way. Cement contents of 8.0 bags per cu yd (450 Kg/m^3) were generally satisfactory with respect to workability. Increase in the cement content to 10.0 bags per cu yd (560 Kg/m^3) produced complete collapse of the fresh concrete at W:C 0.28.

It was estimated that the useful working time of low porosity concrete is between 30 and 60 minutes. Higher water to cement ratios and higher sulfonated lignin content to $NaHCO_3$ content ratios lengthen the useful working time of concrete.

Studies were carried out to investigate some aspects of the hydration process of low porosity cement paste having W:C ratios 0.22, 0.23 and 0.24.

The early hydration processes of low porosity cement paste can be subdivided into three stages. Stage I includes the pre-dormant and the dormant period which include the reactions that occur between the time of first contact between water and cement, and the time when the dormant period ends. Not much heat is evolved in this stage. In Stage II the hydration reactions speed up and considerable heat is evolved, raising the temperature. In the present work a double temperature rise effect was observed within this stage, presumably associated with some effect of the admixtures used. In Stage III the heat evolution rate in the paste decreases continuously.

In these quasi-adiabatic tests the degree of temperature elevation attained by the paste at any stage of hydration was practically independent of its W:C ratio, at least in the W:C range examined. However, the times required to reach the end of the induction period and the top of the hump after this are longer for higher W:C ratios, particularly in the case of the W:C 0.24 paste. The additional times required to reach subsequent characteristic points on the curve are practically independent of the W:C ratio of the paste. It was observed that if the RH of the laboratory air was unusually high, about 75% RH, the completion of the dormant period for paste was somewhat delayed. No such effect was found with concrete.

Parallel testing revealed a close relationship between the time of setting of low porosity cement paste and the occurrence of the minimum point of the first stage on the corresponding temperature evolution curve. In determinations of the time of setting by the Vicat needle penetration, this time coincided with the attainment of the first minimum on the temperature evolution rate curve, i.e., the end of the dormant period, within 10 minutes. Thus, similar to the observation with respect to first minimum occurrence, the time of setting of low porosity cement paste having W:C 0.23 is only slightly longer than that of the W:C 0.22; but the W:C 0.24 paste is significantly longer.

The degree of hydration of low porosity cement paste is low for the first 18 hours or so, but then increases rapidly and reaches about 80 % of that for the mature condition in 2 days. The estimated degree of hydration of "mature" (90 day) low porosity cement pastes was about 62%, obviously limited by space considerations.

Studies of the microstructure and composition of low porosity cement paste W:C ratio between 0.22 and 0.24 were made at several ages up to 90 days by SEM, DTA and XRD. Low porosity cement pastes at early stages of hydration do not develop the obvious AFt hydration products formed in ordinary gypsum-bearing cement pastes. At the time of setting (6 1/2 hours), there is little change in microstructural appearance of the paste as compared to the unhydrated cement, but a trace of $Ca(OH)_2$ was detected by DTA and some evidence of C-S-H gel may be inferred from the endotherm observed between 100°C and 300°C. By 15 hours hydration products appear all over the paste surrounding residual grains of ground clinker. Hydration products in the form of small thin particles, thin plates (AFm phase?) and a very few elongated hydration products (AFt phase?) are distinguishable. At 24 hours higher concentrations of hydration products may be seen all over. Particles tentatively identified as C-S-H gel Type III are prominent and a few elongated particles are present. Much of the hydration product seems massive and even-textured. Apparent embedded crystals of $Ca(OH)_2$ are detectable by SEM and XRD and DTA confirm the presence of significant amounts of this compound. By 2 days SEM micrographs indicate that most of the hydration products have fused into a mass with individual particles mostly not separable.

DTA results show stronger endothermal effects for C-S-H gel and $Ca(OH)_2$. Subsequent changes in morphology are minor, but increasing amounts of C-S-H gel and of $Ca(OH)_2$ may be inferred from XRD and DTA results. The hydration products of low porosity cement paste are basically the same as those formed in gypsum-bearing cement systems: C-S-H gel and crystalline $Ca(OH)_2$. However, there are some differences: (a) the microstructure becomes massive at an early stage, (b) significant quantities of Type I or Type II C-S-H gel are never observed, (c) no ettringite is formed and few elongated particles develop, and (d) there are DTA effects peculiar to the system. Studies on low porosity cement paste hydrated at W:C 10 in a rotary container indicated that at least some of the differences just mentioned may be due to the effect of the low W:C (0.22 - 0.24) ratio used rather than the effect of the chemistry of the admixtures that replace the gypsum.

High pressure mercury intrusion experiments carried out on a W:C 0.24 low porosity cement paste suggested that low porosity cement paste is tighter and less porous than ordinary Portland cement paste at any given age.

Permeability measurements indicated that low porosity cement paste is much less permeable than ordinary Portland cement paste for all W:C ratios by a factor of the order of magnitude of 10.

Compressive strength determinations were made on low porosity cement pastes having W:C 0.22, 0.23 and 0.24. The compressive strengths of the paste recorded at one day were about 66 MPa (9,5000 psi) except that W:C 0.24 were somewhat weaker, reflecting slower hydration. Subsequently the compressive strengths of the paste were not very different in terms of comparison between the different W:C ratios. At 28 days the compressive strength of the paste was about 117 MPa (17,000 psi).

Compressive strength determinations for low porosity concrete were made for W:C 0.26 to W:C 0.32 at ages ranging from 1 day to 28 days, with a few determinations at 90 days. Most of the concretes examined had a cement factor of 8.0 bags per cu yd (450 Kg/m^3) and an aggregate cement ratio of around 4. The results show that compressive at any age are relatively unaffected by W:C ratios between 0.26 and 0.30 but that a significant decrease in compressive strength at early ages is obtained when the W:C ratio is increased to 0.32. By 90 days, however, all concretes have a similar strength value of about 76 MPa (11,000 psi). The general levels of compressive strengths reached by these low porosity concretes at 2 days were about 39 MPa (5,700 psi); at 7 days were about 63 MPa (9,000 psi), and at 28 days were about 70MPa (10,000 psi), with somewhat higher values developed in special trials.

It was found that variations in the sulfonated lignin content did not affect the compressive strength of low porosity concrete.

Variations in the $NaHCO_3$ content influenced the compressive strength of low porosity concrete at early ages, but differences disappeared by 7 days.

Trial mixes with cement factor reduced to 7.0 bags per cu yd (390 Kg/m^3) and W:C ratios of 0.28 were made, but consistency and flow properties were unsatisfactory and no specimens were cast for testing. Mixes cast with cement factor 10.0 bags per cu yd (560 Kg/m^3) reducing the aggregate to cement ratio to 3.0, were found to be only slightly stronger than the 8.0 bags per cu yd (450 Kg/m^3) mixes at any given age.

Flexural strength tests carried out at 28 days on low porosity concretes having W:C 0.26, 0.28 and 0.30 indicated that the flexural strength of low porosity concrete is not affected by it W:C ratio in this range studied. The values obtained were about 8.4 MPa (1,220 psi). The dynamic modulus of elasticity of these concretes were found to be around 59,000 MPa (8.6×10^6 psi) which is considerably higher than the expected for high-strength concrete of similar compressive strength made with conventional Portland cement.

CHAPTER VI

CONCLUSIONS

1. Cement pastes that flow easily without vibration can be made at as low a W:C ratio at 0.23 using low porosity cement: a finely ground gypsum-free clinker, regulated with an admixture of sulfonated lignin and sodium bicarbonate instead of the usual interground gypsum.

2. Concrete made with low porosity cement reflects much of the rheological behavior of its constituent paste. It is possible to produce "low-porosity concrete" that flows easily without vibration at as low a W:C ratio as 0.28. Such concrete yields slumps of the order of 205 mm (8 in.) and Vebe times of the order of 5 seconds.

3. The workability of low porosity concrete is affected by variations in its W:C ratio, admixture content, and cement content.

4. Relatively small water content variations in low porosity concrete have a marked influence on its flow and workability properties. Free-flowing, "self-compacting" properties can be observed for concretes of W:C 0.30 or greater, and such concretes collapse completely in the slump test. Reduction in water content to approximately W:C 0.28 causes the concrete to remain free

flowing but to require some slight compactive effort. Further reduction in water content down to W:C 0.26 produces mixes that require considerable vibration to consolidate properly.

5. Variations in the $NaHCO_3$ content affect workability only if this admixture is added in large amounts, of the order of 1.4% or greater.

6. Variations in the sulfonated lignin content above some minimum amount have little influence on the workability properties of low porosity concrete, the minimum amount being of the order of 0.6%.

7. The cement content of the concrete has a marked influence on its flow and workability properties, when compared at a given W:C ratio. About 8.0 bags per cu yd (450 Kg/m^3) are required for staisfactory behavior; increased cement contents produce increased apparent fluidity.

8. Low porosity concrete having W:C ratios between 0.26 and 0.32 show little or no segregation.

9. The useful working time of low porosity concrete varies between 30 and 60 minutes depending on its W:C ratio, and on the relative proportion of the admixtures. Higher W:C ratios and higher sulfonated lignin: $NaHCO_3$ ratios lengthen the working time of concrete.

10. The fluidity exhibited by low porosity concrete may provide considerable savings in time and costs in

construction because of the limited need for compaction equipment and because of associated time and energy savings. On the other hand, fluidity may be a restrictive factor for its use in concrete members whose surfaces not in contact with the forms deviate from horizontal. However, adjustment of the W:C ratio to a lower value may prevent any such difficulty.

11. The time of setting of low porosity cement paste is closely related to its temperature evolution curve, and coincides with the end of the dormant period exhibited in the curve.

12. The time of setting of low porosity cement paste and the corresponding phenomena associated with set are affected by high levels of RH in the ambient air, values greater than RH 75% causing delay in the time of setting of the paste.

13. Low porosity cement pastes at low W:C ratio levels and under normal conditions develop relatively high degrees of hydration, and mature microstructural characteristics at early ages.

14. Low porosity cement paste and low porosity concrete, both made at low W:C ratio levels, develop relatively rapid strength gain and high compressive strengths.

15. The compressive strength of low porosity concrete is affected significantly by variations in its

W:C ratio. It is influenced by $NaHCO_3$ content only at early ages, and is insensitive to variations in cement content (in the range explored) and to variations in sulfonated lignin content.

16. Optimum concentrations of the present low-porosity cement admixtures, considering both fresh concrete behavior and the strength developed for hardened concrete are of the order of 1.2% $NaHCO_3$ and 0.7% of the sulfonated lignin.

17. The flexural strengths and the dynamic modulii of elasticity of low porosity concretes are considerably higher than the corresponding values observed by others with high-strength concrete.

18. The high strength levels and early strength development shown by low porosity concrete may introduce considerable savings in concrete construction. The attainment of high compressive strengths ar early ages without external aids suggests that low porosity concrete may permit early form stripping and early use of concrete at the job site and in precast concrete plants. In addition, low porosity concrete may meet the load requirements of a structural design with thinner concrete sections than would be needed for high-strength concrete made with ordinary Portland cement.

19. Low porosity concrete is likely to be more durable than ordinary Portland cement concrete.

Permeability measurements and pore size distribution determinations indicated that low porosity cement paste is significantly less porous and less permeable than ordinary Portland cement paste. The potential superiority of low porosity concrete for highway bridge decks is thus indicated.

20. Because of the delay in strength gain exhibited over the first day or so, for low porosity concrete, it does not appear that such concrete will be useful in highway patching applications or other such applications calling for rapid strength development over the first few hours.

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