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PSU/WES INTERLABORATORY COMPARATIVE METHODOLOGY STUDY OF AN EXPERIMENTAL CEMENTITIOUS REPOSITORY SEAL MATERIAL

Report 2

FINAL RESULTS

by

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March 1982

Report 2 of a Series

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Two separate laboratories are investigating the possible use of portland-cement grout as a repository sealing material for underground isolation of nuclear waste. The laboratories are the Materials Research Laboratory of The Pennsylvania State University (PSU) and the Structures Laboratory (SL) of the U. S. Army Engineer Waterways Experiment Station (WES). The project manager, Mr. Floyd L. Burns of the Office of Nuclear Waste Isolation (ONWI), suggested

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20. ABSTRACT (continued).

that these laboratories make a comparative study to determine their ability to obtain results of similar precision and accuracy on potential repository seal materials. This report gives the results of this study.

The same cementitious grout mixture was prepared in each laboratory in September 1980, and tests were started. Tests included characterization of cement and fly ash by chemical, physical, x-ray diffraction, and other procedures. Tests of hardened specimens included restrained expansion, compressive strength, modulus of elasticity, density, and permeability and characterization by x-ray diffraction and scanning electron microscopy. Each laboratory made many of the same tests and some that were not directly comparable.

This report supersedes ONWI-198 (WES MP SL-81-2), which was preliminary in nature. The present report contains all results of the study.

The objectives of the study were to:

(a) Develop a plan which would contribute to ensuring reproducibility of diagnostic methods used in research and development on repository sealing materials.

(b) Compare results of tests performed by similar methods on similar cementitious seal materials, conducted and prepared in each of the two laboratories.

(c) Use the results of complementary, but not identical, tests performed in the two laboratories to confirm the validity of performance-related information gained.

(d) Generate data on a plugging material which could be a candidate for repository sealing in halite or anhydrite host formations or formations containing both halite and anhydrite.

There was generally good agreement between the results of the tests that were performed by both laboratories. This provided confidence in their ability to reproduce the results of tests and characterizations. The results indicated that the starting materials received from a common source were highly similar as evaluated in the two laboratories. In the past this has not always been the case. The similarity was possibly better because of the fact that certain of the materials were received by SL, the lots divided and part shipped to PSU. There was also the added accomplishment that where non-identical methods were used in the two laboratories, some provided complementary types of information which in some cases confirmed that the selected proportions for an experimental grout mixture would be satisfactory from a broader range of considerations, both relating to early-age behavior and having implications for longevity in performance.

Preface

The work described in this report was done by the Structures Laboratory (SL) of the U. S. Army Engineer Waterways Experiment Station (WES) and by the Materials Research Laboratory of The Pennsylvania State University (PSU). That done by the SL was funded by the U. S. Department of Energy through the Office of Nuclear Waste Isolation, Battelle Memorial Institute, under Contract No. DE-AI97-81ET46633. The work done at PSU was under Subcontract No. E512-04200 with Battelle Memorial Institute, Project Management Division.

This is Report 2 of a series and presents the final results of the study. Report 1 presented the short-term results.

Mrs. Katharine Mather was Project Leader for the work done at SL under the general supervision of Mr. Bryant Mather, Laboratory Chief. SL personnel who aided in performing the work were A. D. Buck, J. E. Rhoderick, J. P. Burkes, J. H. Ahlvin, J. A. Boa, Jr., R. E. Reinhold, R. E. Richter, D. M. Walley, and W. G. Miller. Mrs. Mather and Mr. Buck prepared the parts of this report dealing with SL work.

Dr. Della M. Roy was Project Leader for the work done at PSU. PSU personnel who aided in performing the work were M. W. Grutzeck, P. H. Licastro, E. L. White, L. D. Wakeley, D. Wolfe-Confer, A. Kumar, B. E. Scheetz, A. Rousan, K. Ogawa, M. Perez, M. Gharib, and Z. Chang. Dr. Roy and Dr. Grutzeck prepared the parts of this report dealing with PSU work.

Technical Project Officer for all the work was Mr. Floyd L. Burns of ONWI.

COL T. C. Creel, CE, was Director of WES during this period. Mr. F. R. Brown was Technical Director.

PSU/WES INTERLABORATORY STUDY OF
AN EXPERIMENTAL CEMENTITIOUS
REPOSITORY SEAL MATERIAL

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PSU/WES INTERLABORATORY STUDY OF AN EXPERIMENTAL CEMENTITIOUS REPOSITORY SEAL MATERIAL

1.0 Introduction

1.1 Background

The Office of Nuclear Waste Isolation (ONWI) proposed a joint interlaboratory study* as a supplement to ongoing studies of cementitious materials mixtures for borehole plugging and shaft and tunnel sealing. This is part of a continuing effort to ensure high-level reliability of experimental studies carried out in that part of the Department of Energy's (DOE) National Waste Terminal Storage Program concerned with repository sealing materials. The concept and details of the study were subsequently agreed upon by The Pennsylvania State University (PSU) and the Structures Laboratory (SL) of the Waterways Experiment Station (WES) and work was started during FY'80.

The work done at WES was conducted in accordance with the proposal "Investigation of Composition, Constitution, Properties, and Interactions of Materials Considered for Use in Plugging Boreholes and Shafts in Connection with Nuclear Waste Isolation," funded by the Department of Energy effective January 1980 at the SL, in which it is stated: "The third objective of the WES FY'80 program will be the development of precision and accuracy data on the methods used in the evaluation and characterization of the basic materials and grout mixtures. This work will be done jointly with The Pennsylvania State University (PSU) and will involve exchange of samples and specimens. Milestone No. 3 will be a joint PSU/WES report on precision and accuracy of methodology."

The cementitious mixture formulated for the comparative study was intended for possible application to sealing boreholes in halite, anhydrite, or adjacent members of bedded evaporites. The mixture selection used results from studies of the Bell Canyon BCT-1F and BCT-1FF mixtures(1,2) previously carried out as an adjunct to the placement of an experimental field borehole plug.(3) This mixture was designed for potential compatibility with anhydrite, yet compatible with more saline environments.

---

*Proposed by Mr. Floyd L. Burns, Project Manager in the Engineering Development Department of the Office of Nuclear Waste Isolation during a planning meeting in Atlanta, 22-23 August 1979.

In conducting the joint study, efforts were made to ensure that, insofar as possible, starting materials were from the same lots and that testing procedures were well documented. Whenever possible, both laboratories used published and well established test procedures such as those of the American Society for Testing and Materials (ASTM),(4) The American Petroleum Institute (API),(5) or handbooks,(6) and manuals. When no referenceable procedures existed, or changes were made to established techniques, these are documented. The investigation consisted of: (a) comparative studies in which similar, if not identical, tests were carried out in both laboratories, and (b) supplemental tests or experiments in which each laboratory performed specialized tests intended to provide information or data describing the same phenomenon or aspect of performance.

1.2 Objectives

The objectives of the study were to:

(a) Develop a plan which would contribute to ensuring reproducibility of diagnostic methods used in research and development on repository sealing materials.

(b) Compare results of tests performed by similar methods on similar cementitious seal materials, conducted and prepared in each of the two laboratories.

(c) Use also the results of complimentary, but not identical, test methods performed in the two laboratories, to illustrate the confirmative performance-related information gained.

(d) Generate data on a material which could be a candidate for repository sealing in halite or anhydrite host formations, or those containing both halite and anhydrite.

1.3 Reporting Method and Format

Reporting format and treatment of numerical data generally complies with form and principles given in ASTM C 802(4) and E 177(4) as applicable. The report deals with experimental and test procedures and then with results. The latter include tests and characterization of starting materials, and results of tests of specimens at ages up to one year. The report also includes, where applicable, a summary of findings regarding accuracy and precision of data collected during the interlaboratory study and recommendations for improvement.

Throughout this report, numerical values are given in the units in which the measurement or designation was determined or established. If this was in SI units* a calculated converted value is not usually given; an exception is made where the SI value, though primary in the U.S., is not well known, as for example "45-μm (No. 325) sieve" or the use of Angstroms rather than nanometers for x-ray diffraction spacings. When the value was determined or established in other than SI units, a calculated SI value is usually given. The calculated SI equivalent often is not correctly rounded since not in all cases can the precision of the non-SI value be reasonably estimated, a prerequisite to rational rounding.

1.4 Interim Report (ONWI-198)**

An interim report, ONWI-198 (WES MP SL-81-2), dealing with short-term results, was issued in September 1980.*** In addition, both laboratories had scheduled compressive strength tests and examinations by x-ray diffraction to the age of one year. At SL, WES, restrained-expansion bars were also measured to at least one year. PSU did long-term SEM and permeability testing. The present report is a final report and as such supersedes ONWI-198 (WES MP SL-81-2). It incorporates both the results given in the former report and those obtained later.

---

*See ASTM E380-79 Standard for Metric Practice.(4)

**ONWI 198, Roy, D.M., M.W. Grutzeck, and K. Mather, PSU/WES Interlaboratory Comparative Methodology Study of an Experimental Cementitious Repository Seal Material, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, 1980.

***The date of the revised version of WES MP SL-81-2 is "March 1981."

2.0 Materials Used and Their Sources

2.1 Background

At both PSU and WES, each of the materials used in this study was derived from the same source. Slight variability might be expected as a result of post-shipment handling procedures, but these were found to be generally negligible.

2.2 PSU

Upon receipt, materials were logged in and inspected for shipping damage. If in airtight containers, the containers were labeled and the material maintained in the original container. If in bags or other non-airtight containers, the material was transferred to airtight plastic pails.

Materials used at PSU are described below:

(a) Class H cement (PSU #H-7) - three bags received 12 June 1980 directly from Lone Star Industries, Inc., Maryneal, Texas. Transferred to airtight plastic pails.

(b) Fly Ash (PSU #B26) - Received from WES (J. Boa) 16-21 April 1980. High-lime fly ash from western coal.

(c) Expansive Additive (PSU #A31) - Received from WES (J. Boa) 16-21 April 1980.

(d) NaCl (PSU #B08) - Reagent grade NaCl.

(e) Water Reducer (PSU #A28) - Received May 1979. High-range water-reducing admixture ("superplasticizer"), naphthalene-sulfonate condensate.

(f) Defoaming Agent (PSU #A27) - Received May 1979.

(g) Deionized Water (PSU #E11)- Freshly boiled and stored in a collapsible water container equipped with a spigot.

2.3 WES

Materials received at the SL are identified, the date of receipt recorded, serial numbers assigned, and the samples inspected and labeled. Cement, fly ash, and expansive additives are stored in plastic bags in steel drums.

Materials used at WES included the following:

(a) WES RC-853(2), three bags of Class H cement from the Maryneal plant of Lone Star Industries at Sweetwater, Texas, received 11 June 1980, stored in plastic bags in 30-gal steel drums.

(b) WES AD-592(4), a 55-gal drum of fly ash from the Harrington plant of Southwest Public Service, Amarillo, Texas, received 13 February 1980.

(c) WES AD-626, an expansive admixture stored in a 55-gal drum, received 13 February 1980.

(d) AD-627, an experimental water-reducing admixture, received 13 February 1980; a naphthalene-sulfonate condensate.

(e) WES AD-599, a defoamer, received 2 April 1979.

(f) Mixing water, deionized, boiled, and stored, in closed containers that are clean, filled, and well stoppered.

(g) WES AD-640, 13,000 lb of Carey's Coarse Granulated Salt, in 50-lb and 100-lb bags, from the Vicksburg Cooperative, Vicksburg, Mississippi, received in early January 1977. A sealed 50-lb bag was chosen to furnish salt for use in this program. Salt from this lot has been used to make both saturated and 30% sodium chloride solution for mixing and testing salted grouts expected to be used in salt beds.

3.0 Characterization Methods for Cement and Fly Ash

3.1 Chemical Analyses

Chemical analyses were performed by both laboratories and results were reported as detailed below.

3.1.1 PSU - Chemical analyses for cement and fly ash include determinations made in accordance with ASTM C 114(4), and C 311(4) as applicable. Methods used were:

SiO_2 - Referee method of ASTM C 114 including the volatilization with HF of the SiO_2 to recover the residue.

CaO - Aliquots of the filtrate from the silica determinations are titrated for Ca at pH 12 by EDTA.

SO_3 - An instrumental method using the Leco Induction Furnace and the Leco Semi-Automatic Sulfur Titrator. Total sulfur is reported as SO_3.

Al_2O_3
Fe_2O_3
MgO
Na_2O
K_2O
TiO_2
P_2O_5
Mn_2O_3
BaO
SrO

} Emission spectrometric analysis (ESA) by Spectrometrics, Inc., plasma emission spectrometer.

LOI - The sample is ignited in a platinum crucible in a muffle furnace at a temperature of 950° ± 50°C to constant weight (ASTM C 114 referee method).

CO_2 - A gravimetric method in which the carbon dioxide in the sample is released by phosphoric acid and is collected in weighing bulbs containing ascarite.

3.1.2 WES - Complete chemical and physical tests are performed according to procedures outlined in the Handbook for Concrete and Cement(6) and in other references. Chemical analyses were made using ASTM C 114(4) as applicable. Procedures for cement and fly ash analyses were similar, except that Al_2O_3 and Fe_2O_3 analyses for the fly ash were done by atomic absorption (AA) as was done for the cement but is not referenced in ASTM C 311. The cement [RC-853(2)] was analyzed for Al_2O_3, Fe_2O_3, Mn_2O_3, P_2O_5, TiO_2, SrO, BaO, CaO, SiO_2, MgO, SO_3, Na_2O, K_2O, LOI, and insoluble residue. Al_2O_3 and Fe_2O_3 were determined both by wet methods and by AA methods. P_2O_5, BaO, and SrO were determined by emission spectrometric analysis using a Spectrometrics, Inc. plasma emission spectrometer in the WES Environmental Laboratory.

3.2 Density

Density was determined on both cement and fly ash by both laboratories.

3.2.1 PSU and WES - ASTM C 188(4) (Le Chatelier Flask) was used to measure density. For fly ash determination, a 50-g sample of fly ash was used instead of the required 64 g used for cement.

3.2.2 PSU - In addition, density was also determined by ASTM C 329(4) using distilled kerosene and a 25-mL pycnometer.

3.3 Fineness by Air-Permeability Method

Fineness of both cement and fly ash was determined by both laboratories using ASTM C 204(4). The sample used for the fly ash determination was of different mass than that used for the cement determination.

3.4 Fineness by Wet Sieving on a 45-μm (No. 325) Sieve

Fineness determinations by wet sieving on a 45-μm (No. 325) sieve were carried out on both cement and fly ash, according to ASTM C 430(4).

3.5 X-ray Powder Diffraction

X-ray powder diffraction scans for both the cement and fly ash were obtained and are reported as a tabulation of d-spacings and associated intensities.

3.5.1 PSU - Each material was scanned using a Philips APD-3600 x-ray diffractometer, which had been standardized against a silicon metal standard. Scans were accomplished in increments of $0.02°2\theta$, at two different counting times: 1.2 sec per increment, and 0.6 sec per increment.

3.5.2 WES - Two scans were made for each material: a fast scan at $2°2\theta$/min and a slow scan at $0.2°2\theta$/min. A GE XRD-700 x-ray diffractometer was used.

The XRD-700 spectrogoniometer was replaced in May 1980 by an XRD-5 spectrogoniometer which corrected the tendency of the XRD-700 goniometer to lose synchrony with the recorder. All patterns were made using an approximately logarithmic intensity scale. The daily standardization procedure is given in the two parts of Enclosure 1 to Appendix B.

3.6 Early Heat of Hydration

3.6.1 PSU - Early heat of hydration was determined with a series of three thermopile-equipped calorimeters set to operate isothermally at 38°C. A 2-g sample of solid material homogeneously mixed in a Spex mill for 20 min was uniformly distributed in a stainless steel cup which fit snugly into the calorimeter. In order to guarantee uniform distribution of the liquid over the sample, a piece of filter paper with five holes in it was cut to fit over the sample. The loaded container was put into the calorimeter, and the unit was assembled. A syringe was filled with 0.3 mL of the liquid portion of the mixture and it was put into the proper calorimeter recess and the entire unit was allowed to come to thermal equilibrium. After injection of the fluid, the heat of reaction was followed on a strip-chart recorder. The results reported were confirmed by three replicates in each instance.

4.0 Mixture Formulation and Viscometry

4.1 Background

The original mixture was formulated by PSU and the formula was given in a letter dated 31 March 1980. Modifications to the original mixture were suggested by WES in a letter dated 18 April 1980. Planning was begun in January 1980 and completed, except for minor revisions, in August 1980.

4.2 Preliminary Testing

The following procedures are normally used in the two laboratories in connection with selecting proportions for mixtures and were used in the current study, with individual details for this specific situation.

4.2.1 PSU - Three series of preliminary tests were performed.

(a) Viscometry - A series of tests was made at PSU using a Haake Rotovisco RV III Viscometer equipped with a serrated rotor and a cup (SV II P). For the present study, slurries formulated with deionized water and saturated $CaSO_4$ solution, respectively, were tested using an accelerating rotation rate of 100 RPM/min. Pastes were run from 0 to 630 to 0 RPM as a function of the age of the paste (up to 2 hr)(7,8).

(b) Zeta Potential - Measurements of zeta potential were made at PSU using an electrophoretic method and a zeta meter. The method has been described elsewhere.(7) Normally, the cement is dispersed in a dilute suspension. Both deionized water and saturated $CaSO_4$ solution with varying concentrations of water-reducer (A28) were used as alternate media.

(c) Compressive Strengths - Preliminary compressive strength measurements were made. ASTM procedures were followed with slight modifications in mixing and molding procedures (see Sections 5 and 6 for details).

4.2.2 WES - In addition to the other preliminary tests used in both laboratories, preliminary testing at WES included tests using the flow cone (CRD-C 79-58, now known as CRD-C 611)(6) to establish that the grout was appropriately flowable.

4.3 Final Mixture Proportions

Data obtained as a result of preliminary testing were used in arriving at a final mixture formulation. Since there were minor problems associated with the use of a saturated $CaSO_4$ solution as mixing water (higher apparent viscosity, less flow, gummy deposits which were relatively harder to remix, lower compressive strengths, Class H cement particle flocculation), and the potential for solution of the anhydrite host rock by deionized water during early stages of paste hydration still existed, a third formulation was agreed upon. The final version given in Table 4.1 used deionized water and additional dry $CaSO_4 \cdot 1/2\ H_2O$ added to the mixture to aid in the saturation process and perhaps reduce the potential for anhydrite host-rock solution.

Table 4.1. Mixture Proportions.

a. PSU Mixture Proportions (#80-081)

Material	PSU ID #	Grams	mL	
Class H Cement	H-7	68.00		Preblended Dry Solid Material
Fly Ash	B26	22.90		
Expansive Additive	A31	8.34		
NaCl	B08	4.05		Premixed Solution
Water Reducer	A28	1.099		
Defoaming Agent	A27		0.02	
Freshly boiled dionized water	E11	29.4		

b. WES Mixture Proportions.

	Trial Batch Mass, g	Mass, %	Mass, g, for 0.1 cu ft (0.0028 m^3)	Batch Mass, g
Cement H (RC-853(2))	68.0	50.84	2960	7831
Flyash (AD-592(4))	22.9	17.12	997	2637
Expansive Admixture (AD-626)	8.3	6.20	364	963
NaCl (AD-640)	4.05	3.03	176	467
Water Reducing Admixture (AD-627)	1.10	0.82	48	126
Defoamer (AD-599)	0.02 mL**	0.01		1.5
Water (Deionized/or distilled and boiled)	29.4	21.98	1280	338.6
	133.7	100.00	5825.58	15411.5
Expansive Admixture (AD-626)	(2.5)			
	(136.2)			

*Added to saturate mixing water with $CaSO_4$. The 2.5 g is the amount first added for 0.1 cu ft (0.0028 m^3); thus it is obviously wrong for a mixture with a mass of 133.7 g, and consequently it is not included in a revised total or the mass, %.

**Assuming specific gravity = 1, a close approximation, as mass %.

5.0 Mixing Procedure

5.1 Introduction

A standard mixing procedure is important in ensuring reproducibility of performance of grout samples. In order to have a valid interlaboratory comparison, the mixing procedure followed by both laboratories was similar.

5.2 PSU

The following mixing procedure was used for preparation of all mixtures proportioned as shown in Table 4.1a.

(a) In all cases the deionized water was freshly boiled in a stainless steel container, cooled and stored in a tightly stoppered collapsible plastic bottle, keeping it as full as possible to prevent absorption of CO_2 from air space above water.

(b) In all cases the dry solid materials (Table 4.1a) were weighed into a Pyrex beaker of sufficient size to make blending by hand efficient. Dry solids were blended until of uniform color.

(c) Freshly boiled (FB) deionized water was weighed and placed into the mixing bowl of a Hobart mixer. The water reducer (PSU A28) was added to the water and dissolved. NaCl and defoaming agent (PSU A27) were added and dissolved.

(d) Dry materials were added to the premixed solution (see Table 4.1a) in the mixing bowl. ASTM C 305(4), Section 5 mixing procedure, was followed from this point, except that the mixing bowl was covered.

5.3 WES

The grout, proportioned as shown in Table 4.1b, was mixed in a Hobart mixer. After measuring out the needed masses of cement, fly ash, expansive admixture (AD-626), NaCl, and water-reducing admixture, they were pre-blended. The measured mixing water and defoamer were added to the clean bowl. The solids were added gradually to the water and defoamer while the mixer was operating at slow speed. The mixer was operated at slow speed with the stainless steel wire whip for 1 min. The mixer was stopped and the inside of the bowl was scraped down and the mixture was allowed to rest for 30 sec total including the scrape-down time. The mixer was started at slow speed and operated for a total elapsed time of 5 min. The flow cone was filled; the thumb was removed from the opening at the bottom of the flow cone at 6 min and the flow time was measured according to the CRD-C-79-58 (now CRD-C 611)(6). The material used to determine flow time was returned to the mixing bowl and remixed for 15 sec. It had been intended to mix the grout following ASTM C 305, using the stainless steel paddle called for there. However, it was found that the paddle splashed grouts of fluid consistency out of the bowl. Therefore, the mixing procedure described above, using a wire whip which can be purchased from the manufacturer of the mixer, was used.

6.0 Molding and Curing Procedures

6.1 PSU

Six types of samples were cast. The following sections deal with their preparation and curing. Figure 6.1 summarizes the nature of the samples cast at PSU and their ultimate ulilization.

6.1.1 Cube Specimens - The bottom plate of a standard three-compartment 2-in (50.8-mm) bronze cube mold was sealed with a layer of high-vacuum grease. The interior of the molds was coated with two layers of a Teflon non-stick spray. The molds were filled according to ASTM C 109 (4)*. After filling, the three-compartment mold was covered with a plate-glass cover, again secured with vacuum grease and held in place with thick rubber bands. The molds were completely immersed in tap water for 24 ± 1/2 hr at 38°C. After this period the samples were demolded, density was measured, and specimens were immersed in saturated $Ca(OH)_2$ solution and allowed to cure at 38°C.

6.1.2 One-Inch (25.4-mm) Diameter by Two-Inch (50.8-mm) Long Cylindrical Specimens - These were cast in similarly prepared seven-compartment brass molds fabricated at PSU. They were filled to 1/2 of their depth and puddled with a thin steel rod, paying special attention to the cylinder walls. The cylinder was then filled to the top, similarly puddled, and struck off with a trowel. These molds were then covered with brass plates which were sealed with grease and held in place with rubber bands. They were then completely immersed in tap water for 24 ± 1/2 hr at 38°C. After the specimens were demolded and the specific gravity measured, they were immersed in saturated $Ca(OH)_2$ solution, and allowed to cure at 38°C.

6.1.3 Samples Cast in Glass Shell Vials - These were fitted with air-tight tops (Parafilm M). The glass vial was first coated with two coats of Teflon spray allowing each to dry before proceeding. The paste was introduced and puddled as were the cylinder molds described in Section 6.1.2. The cylinders

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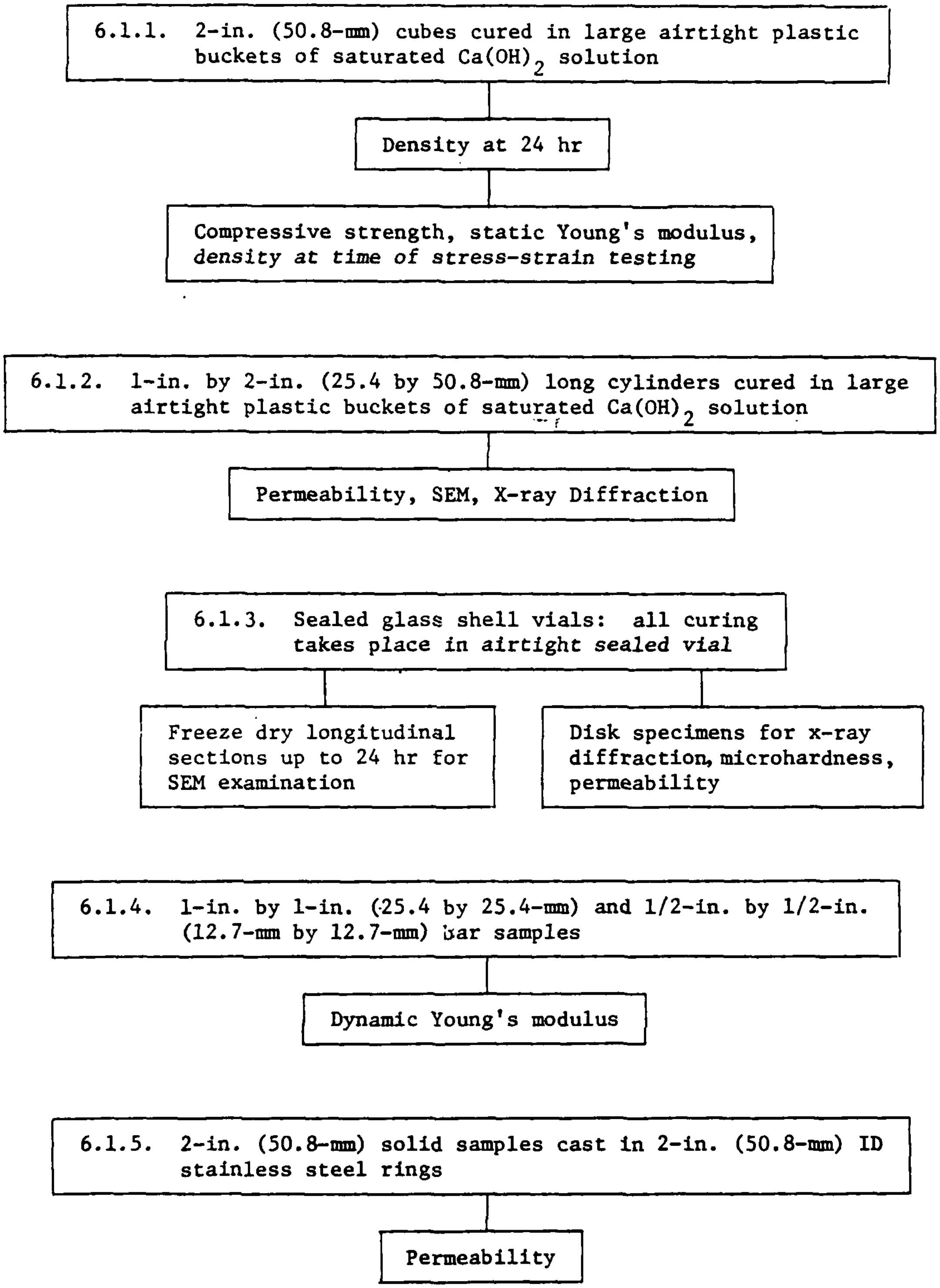
*The molds were filled to 1/2 their depth and puddled with the prescribed ASTM puddler. Once filled to the top, a thin steel rod was used to puddle to prevent overflow.

Figure 6.1. Flow chart depicting testing of Section 6 samples at PSU.



were completely filled, sealed with two layers of Parafilm M, secured with rubber bands, and allowed to cure at 38°C.

6.1.4 Bar Specimens - Specimens with dimensions 1 by 1 by 11-1/4 in. (25.4 by 25.4 by 285.75 mm) were prepared similarly to the cube specimens (Section 6.1.1) using molds described in ASTM C 490.(4) A single specimen was cut to 1/2 by 1/2 by 4-in. (12.7 by 12.7 by 101.6-mm) and three specimens were cut to 1 by 1 by 5-in., 8-in., and 10-in. (25.4 by 25.4 by 127-mm, 203.2-mm, and 254-mm) after curing which was either at 38°C or at 60°C in saturated $Ca(OH)_2$ solution. Measurements were made on these bars at periodic intervals as they continued to cure in $Ca(OH)_2$ solution at their respective temperatures [1/2-in. (12.7-mm) bar at 38°C, 1-in. (25.4-mm) bars at 60°C].

6.1.5 Permeability Specimens - Samples were prepared by casting paste into machined and thoroughly cleaned stainless steel rings having an ID of 2-in. (50.8-mm) and an OD of 2-1/4-in. (57.2-mm). The height of the specimen was nominally 1-in. (25.4-mm). Grout was poured in and puddled. The specimens were fitted with tightly fitting Teflon end caps (top and bottom of cylinders), and immersed in deionized water for the 38°C curing period. In addition, smaller specimens cast as cylinders and cured in $Ca(OH)_2$ or sealed shell vials, were also tested for permeability. These were cut from Section 6.1.2 and 6.1.3 cylinders and were epoxied into metal rings before testing.

6.2 WES

From two batches of grout made on 23 September 1980 the following specimens were prepared for testing. The two batches had measured flows of 14.8 and 14.5 sec by the flow-cone method.

6.2.1 Two-inch (50.8-mm) cubes were made to provide tests at 3, 7, 28, 56, 90, 180, and 365 days. The cubes were not consolidated except to reduce air voids, since a flowable grout for use as a seal material would need to self-consolidate. Sealed molds were stored in a water bath at 38°C (100°F) for 24-hr ± 1/2 hr, then stripped. Upon stripping, 24-hr density measurements were made. All specimens were cured at 38°C in a tank of saturated $Ca(OH)_2$ solution. The cubes were tested in compression, loading plane molded surfaces at each age.

A total of 33 cubes were made, six sets of three from one batch, five sets of three from a second batch.

6.2.2 Twelve polyvinylchloride vials of grout were filled, stoppered, and held at 38°C in the tank of saturated $Ca(OH)_2$ solution for SEM and x-ray examination. Each vial held 35 mL of grout.

6.2.3 Six bars of the nominal size: 1 by 1 by 11-1/4-in. (25.4 by 25.4 by 285.8-mm) were molded and held sealed at 38°C for 24 ± 1/2 hr, then demolded. They were cured in the same manner as described in Section 6.2.1. Upon stripping, the 24-hr initial mass and resonant frequency measurements were made. Three of the bars were lost because the molds were inadequately sealed and the grout escaped. Since these bars were made with expansive grout their length was measured and a value of 11-3/8 in. (34.9-mm) was used for L in calculating values for dynamic E.

6.2.4 Two bars, each 2 by 2 by 10-in. (50.8 by 50.8 by 254-mm), for restrained expansion testing were molded in accordance with ASTM method C 806(4). The difference in length between the reference bar and each restraining bar was determined before casting. These molds could not be sealed, hence the specimens were stored at 23°C in the moist curing cabinet rather than in a water bath at 38°C, for 24-hr. After stripping at 24-hr, the bars were stored in saturated $Ca(OH)_2$ solution at 38°C. The first measurement of length change of the bars was made at 24-hr.

6.2.5 Two 6 by 8-in. (152.4 by 203.2-mm) cylinders were molded for permeability tests and cured as described in Section 6.2.1.

7.0 Volume Change Measurements

7.1 PSU

Early volume change was determined by continuous monitoring of a volume of paste in a flexible membrane container.(9) The method is described in more detail in Appendix A1. Preliminary longitudinal dimension change measurements were also made, as described in Appendix A2.

7.2 WES

Restrained expansion was determined at 24-hr to 1 year using the procedures described in ASTM C 806(4) with the exception that the mixture described in Table 4.16 was used rather than the standard mortar.

8.0 Physical and Mechanical Property Testing of Cured Specimens

8.1 Compressive Strength

Compressive strength was measured by both laboratories at 3, 7, 28, 56, 90, 180 (or 181), and 365 days, using 2-in. (50.8-mm) cubes as per ASTM C 109.(4)

8.2 Young's Modulus

Dynamic Young's modulus (E) was determined by both PSU and WES using ASTM C 215(4) at 24 hr. Relative E was determined at later ages. In addition, static Young's modulus was determined at PSU from stress-strain data collected during compression tests.

8.2.1 PSU - Determination of dynamic modulus was made by sonic testing of 1/2 by 1/2 by 4-in. (12.7 by 12.7 by 101.6-mm) and 1 by 1 by 5-in., 8-in., and 10-in. (25.4 by 25.4 by 127-mm, 203.2-mm, and 254-mm) bars of material cured in saturated calcium hydroxide solution at 38°C and 60°C, respectively. The smaller bar was cured at 38°C, but the larger bars were inadvertently cured at 60°C rather than 38°C. Therefore the 60°C data were not comparable with WES data. Determination of static modulus was made from strain data collected during compression testing of cubes using distance between platens as a measure of strain.

8.2.2 WES - Three 1 by 1 by 11-1/4-in. (25.4 by 25.4 by 285.8-mm) bars were removed from the curing tank. The mass and resonant frequency of each was determined and dynamic modulus of elasticity was calculated according to ASTM C 215. They were returned to the curing tank and were tested for resonant frequency again at 3, 8, 28, 56, 90, 180, and 365 days.

8.3 Density

8.3.1 PSU - Density was measured upon demolding and just before testing of 2-in. (50.8-mm) cubes. Density was calculated using a surface-dry mass in air and an immersed mass in water. Values of mass were measured to the nearest 0.01 g. Values were calculated using the formula given below.

8.3.2 WES - Density was measured as the cubes were being stripped. The mass of each cube to be tested was determined in air and water after stripping, using a balance reading to 0.1 g. Density was calculated as follows:

$$\text{Density} = \frac{\text{Saturated Surface-Dry (SSD) Mass in Air, g}}{\text{(SSD Mass in air, g) - (Mass in water, g)}}$$

8.4 Microhardness

Testing of microhardness was done at PSU using the Vickers Method on polished sections of cured cylinders. These data were obtained on specimens cut from Section 6.1.3 cylinders cured in sealed shell vials as a function of time.

9.0 X-ray Powder Diffraction of Cured Specimens

9.1 Introduction

Since both laboratories routinely perform x-ray powder diffraction analysis of cured pastes, d-spacings and intensities as determined at each laboratory are provided.

9.2 PSU

The instrument used was a Philips APD-3600. Samples were scanned in increments of .02° 2θ for 0.5 sec, or approximately 2° 2θ per min. The instrument was standardized against a quartz or Si standard before each use. A standard correction routine was applied to all data files.

Two samples were studied for each test age: paste cured in a sealed shell vial and paste cured in saturated $Ca(OH)_2$ solution. X-ray diffraction patterns were run in both the "as-cured"* and dry state for each sample. X-ray specimens consisted of round disks of cured material cut to fit directly in sample holders designed and fabricated at PSU. As a consequence of the geometry, the data represent information on the interior portions of the samples.

All patterns were run from 2 to 70°2θ using CuKα radiation. Two plots were made: most intense peak full scale; and 300 total counts full scale. In addition, a listing of d-spacings and intensities normalized to the most intense peak were provided.

9.3 WES

Specimens in sealed vials were removed from the curing tank at 3, 7, 28, 56, 90, 181, and 365 days. Each sample was prepared by sawing a 2 by 1 by 1/4-in. (50.8 by 25.4 x 6.35-mm) slab from the center of the vial. The sawed surface was smoothed using methanol until saw marks were gone. Specimens and slabs were kept in methanol and placed in a freezer when necessary to prevent additional hydration and carbonation. X-ray diffraction patterns were made with an x-ray diffractometer using nickel-filtered copper radiation. The sample was placed inside a vapor hood during x-ray diffraction. The hood had an environment of static nitrogen and a sponge soaked with saturated barium hydroxide

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*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

solution. The x-ray diffraction unit was standardized before use each day and a fast pattern (2°/min) and a slow pattern (0.2°/min) were made. See Appendix B for standardization procedures.

10.0 Permeability

10.1 Introduction

Low permeability is one of the most important properties of a prospective borehole or shaft plugging material. However, its measurement is not straightforward and many different techniques exist. In order to begin to quantify and analyze interlaboratory permeability data, detailed descriptions of sample preparation and equipment as well as the actual permeability data are provided by each laboratory.

10.2 PSU

10.2.1 Sample Preparation

10.2.1 Sample Preparation - Samples were prepared using two methods. Stubby cylinders were cut from ∿1-in. (25.4-mm) diameter samples (Sections 6.1.2 and 6.1.3) dried on all surfaces with acetone and ethyl alcohol, coated with epoxy, and sealed into 1-in. (25.4-mm) ID steel rings. Epoxy curing took place in a desiccator with a water reservoir to maintain 100% R.H. Overnight curing was at room temperature.

The second sample was prepared by casting and curing paste in a 2-in. (50.8-mm) ID stainless steel ring about 1-1/2-in. (38.1-mm) high. A container was formed by machining thin Teflon end-caps to fit snugly into the ends of the steel rings. The caps were left in place during curing in saturated $Ca(OH)_2$ solution. Upon testing, the end caps were removed and testing took place with no additional sealing of sample to the steel ring. The bond to the steel was strong enough to support the applied fluid pressure during testing.

In the latter sample, there is no lag time, whereas in the former, the epoxy method, at least 24 hr must elapse before testing due to curing requirements of the epoxy.

In order to ensure a saturated sample before permeability testing, one day prior to testing, the sample was removed from $Ca(OH)_2$ solution, put under freshly boiled deionized water and a vacuum pulled on the sample for 1-1/2 hr with a water tap aspirator. After 1-1/2 hr, the vacuum was released and the sample was returned to the curing chamber in deionized water until ready for testing. Since it was found that samples were "impermeable" under test conditions, this procedure was discontinued after testing of 7-day samples.

10.2.2 Permeability Testing Using Deionized Water - Pressures of 100-400 psi (0.69-2.76 MPa) were used for the 2-in. (50.8-mm) samples and 200-1000 psi (1.38-6.89 MPa) for the 1-in. (25.4-mm) samples. In addition to size, the age of the specimen also dictated the pressures used; the older the specimen, the greater pressure it could support before failing. Pressure was applied in steps starting low and increasing if no permeability was measured in an hour or two.

10.2.3 Flow Rates - Flow rates were recorded on a strip chart recorder as a function of time using collection bottles on a load cell. Output was monitored until it was evident that the slope of the volume vs. time curve was linear and unchanging. Once established, the linear portion of the curve should continue to be linear for at least 24 hr. If no flow was observed after a few days at the highest pressure, the sample was reported as impermeable under the given test conditions: A permeability value (k) darcys* was calculated as follows:

V_1,t_1 = volume (mL) and time (hr) where curve first becomes linear.

V_2,t_2 = volume (mL) and time (hr) at run termination. If possible, V_2-V_1 should be > 5 mL.

Slope of curve = V_2-V_1/t_2-t_1 = mL/hr. Use this value to calculate permeability using Darcy's law:

$$k_{H_2O} = \frac{(\text{Vis of } H_2O)\ (\text{mL/hr})\ (\text{height, cm})}{(\text{Area, cm}^2)(P_2-P_1,\ \text{atm})(3600\ \text{sec/hr})}$$

10.3 WES

A 6 by 8-in. (152.4 by 203.2-mm) cylinder was removed from the curing tank and cut into a 6-in. (152.4-mm) diameter by 6-in. (152.4-mm) long cylinder and tested for water permeability at 8 days age using deionized water. The second cylinder was cut and tested at an age of 29 days.

Testing was in accordance with CRD-C 48-73, "Method of Test for Water Permeability of Concrete"(6). The flow rate was based on the final 5 days of the 14-day test.

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*Darcy x 9.869233 E-13 = square meter

11.0 Microstructure by SEM

11.1 Introduction

In order to correlate observed physical and mechanical properties in cured grout samples, a study of microstructures was made. SEM equipment was different in the two laboratories, but standardizing sample preparation, magnifications, and reporting descriptive material aids in comparing results.

11.2 Sample Preparation

11.2.1 PSU — Sample preparation is essentially identical to that suggested by WES below, except that the sample is freeze dried and coated with gold. Freeze drying was selected because it had been found that vacuum drying at 60°C for up to 15-1/2 hr would cause previously present ettringite to become x-ray amorphous in x-ray diffraction patterns run on essentially identical disks of hydrated cement paste. Freeze drying on the other hand, caused no such change in x-ray samples cured for 56 days or longer.

11.2.2 WES — After curing in a sealed vial, the sample was split transversely and dried in a vacuum at 50°C for up to 15-1/2 hr and stored in a desiccator with silica gel. This temperature was selected because it had been discovered through experimentation that 50°C will dehydrate the ettringite on the outside surface of a sample. However, since a freshly fractured surface is examined, and not the outside surface, this was not a problem. At the time of examination, the sample was broken again to give a convenient sized piece to mount on a sample stub, preferably with the fracture approximately parallel to the long axis of the cylinder. The sample was coated with carbon, then with an 80:20 mixture of gold to palladium.

11.3 PSU

An SEM/ISI DS-130 with Kevex energy-dispersive x-ray analyzer was used. A minimum of two ages were studied (3 and 28 days). Data consisted of photographs taken at standard magnifications of 1000X and 5000X. Observations were listed beginning with the most pertinent and working downward to the least.

11.4 WES

The grout samples at 3, 29, and 365 days were examined by SEM. National Bureau of Standards Standard Research Material (SRM) 484 was used monthly to verify that magnifications were proper. Resolution was checked monthly using Research Material 100 (Appendix B).

12.0 Results of Preliminary Tests

12.1 Viscometric Data (PSU)

Data for the two pastes mixed using deionized and saturated $CaSO_4$ solutions as mixing water measured at 38°C after various periods of time are reported in Table 12.1. Both mixtures were pourable and near Newtonian in behavior, having slight thixotropic pseudoplastic behavior. However, it was observed that the sample with saturated $CaSO_4$ solution as mixing water tended to settle and form a gummy deposit, which was relatively harder to remix. Its apparent viscosity was slightly higher than the deionized-water counterpart at all times and shear rates, and reproducibility of measured results was poorer.

12.2 Zeta Potential (PSU)

The zeta potential of the Class H cement in the presence of varying concentrations of water-reducing admixture (A28) was measured. Data for the two solutions, deionized water and saturated $CaSO_4$ solution, are presented in Table 12.2. The most negative zeta potentials were found in deionized water containing higher concentrations of A28, similar to concentrations used in the final mixture. In previous studies, highly negative zeta potentials were found to be associated with good dispersion, and hence high fluidity. An apparent coagulating effect of the calcium-sulfate saturated water was seen from the fact that particles tended to clump together and move in groups rather than as individual particles, when water saturated with $CaSO_4$ was used for mixing. The zeta potentials for particles suspended in solutions having low concentrations of A28 in deionized water, after 24 hr were found to be nearly the same as the initial zeta potential at 0.25 hr. These observations confirmed the phenomena observed in viscometric measurements that initially saturating the mixing water with calcium sulfate reduced the effectiveness of the water reducer.

12.3 Compressive Strength (PSU)

Preliminary compressive strength measurements were made on a series of test samples formulated according to the 31 March 1980 version (see paragraph 4.1) using both deionized and saturated $CaSO_4$ mixing water. No consolidation methods were used in molding, and a different batch of Class H cement (H-6) from the same manufacturer was used, which was expected to be similar in performance

Table 12.1. Viscometric Data for the 31 March 1980 (see para. 4.1) Mixture Using Deionized and Saturated $CaSO_4$ Solution as Mixing Water.

RPM	Shear Rate, s^{-1}	Shear stress, Pa. 0.25 hr	1.0 hr	1.75 hr
PSU #800954 made with saturated $CaSO_4$ (PSU #E-9) mixing water				
600	468	78	101	137
300	234	34	46	64
200	156	20	28	41
100	78	~9	~14	21
PSU #800955 made with deionized water				
600	468	63	83	122
300	234	28	39	55
200	156	~16	23	33
100	78	~7	~11	~14

Table 12.2. Zeta Potentials for Class H (PSU #H-7) Cement in Deionized Water and Saturated $CaSO_4$ Solution as a Function of Varying Content of A28

Sample No.	Concentration of A28, %	Zeta potential, mV 0.25 hr	2.0 hr	24 hr
Saturated $CaSO_4$ solution				
801032	0.1	-15.15	-13.86	-13.52
801033	0.01	-15.94	-14.26	-12.18
801034	0.001	-11.68	-7.52	-5.15
Deionized water				
801035	0.1	-25.05	-19.01	-16.83
801036	0.01	-16.83	-14.85	-13.86
801037	0.001	-12.52	-15.65	-11.29

to H-7. Results are reported in Table 12.3. In both cases strengths were adequate and compressive strength or molding procedure difficulties were not a factor in choosing one mixture over the other. However, the deionized-water mixture gave higher compressive strength values at both ages.

Table 12.3. Compressive Strengths of 38°C Cured 2-in. (50.8-mm) Unconsolidated Cubes of the 31 March 1980 Mixture Using Deionized Water and Saturated $CaSO_4$ Solution as Mixing Water.

	Compressive Strength			
	3 days		7 days	
Saturated $CaSO_4$ Solution				
strength, psi (MPa)	5594	(38.6)	6022	(41.5)
σ', psi (MPa)	356	(2.45)	300	(2.07)
n	6		4	
Deionized H_2O				
strength, psi (MPa)	6018	(41.5)	7217	(49.8)
σ', psi (MPa)	380	(2.62)	549	(3.79)
n	6		3	

12.4 Flow Cone (WES)

The materials for a 0.1-ft^3 (0.003 m^3) batch were mixed as follows. Distilled water was added to the mixing bowl along with 2.5g of expansive admixture (AD 626), water reducer, salt, and defoamer, mixed 5 min at slowest speed, and allowed to rest for 3 min. Then the three cementitious constituents were added, mixed by ASTM C 305 procedure, and flow cone measurements were made. The flow time was 12.8 sec, which was considered to be within a suitable range for flowability, pumpability, and to be self-consolidating, as it needs to be for the intended use.

13.0 Characterization of Cement and Fly Ash

13.1 Chemical Analyses

Chemical analyses were performed on the Class H cement and fly ash using previously outlined procedures. Data for the cement and fly ash are given in Tables 13.1 to 13.9 and 13.10, respectively. The PSU analyses were done on samples from three different cement storage pails. The three analyses by WES were made on tube samples, one each taken from each bag of their three-bag shipment. Table 13.10 lists the results of a single fly ash analysis by each laboratory for the fly ash used in the study.

13.2 Results of Chemical Analyses

13.2.1 Intralaboratory Precision

Each laboratory made three analyses of the Class H cement; the results are given in Table 13.1. If the data in Table 13.1 were treated as pertaining to three replicate samples of a single cement, the differences between the extreme values in the three results for the constituents subject to maximum permissible differences in results are given in Table 13.2. The WES SO_3 determinations differed by more than the permissible variation in three determinations. Otherwise the differences among the three bags of cement sampled and analyzed were small enough so that it is reasonable to regard the three samples as if they had been three subdivisions of one sample. The observed differences for PSU were within the maximum permissible differences except for Al_2O_3, Fe_2O_3, CaO, and Na_2O.

13.2.2 Reference Comparisons (WES)

Tables 13.3 and 13.4 are the reports by WES to the Cement and Concrete Reference Laboratory (CCRL) on samples 57 and 58, chemical and physical data. Tables 13.5 and 13.6 are the report by CCRL. Comparison of the tables shows that all of the results from WES are well within one standard deviation from the mean found by averaging all of the determinations made of each constituent. This is the level of accuracy consistently found in analyses by WES using CCRL samples.

13.2.3 Cement Report (WES)

Table 13.7 is the complete WES report of chemical and physical tests of

Table 13.1. Chemical Analyses of Class H Cement, %.

	PSU # H-7			WES # RC-853(2)			
	#H7	#H7A	#H7C		Bag #1	Bag #2	Bag #3
Component							
SiO_2	22.3	22.2	22.30	SiO_2*	22.20	22.24	22.24
$Al_2O_3^s$	3.84	3.87	3.76	Al_2O_3**	3.73	3.70	3.73
				Al_2O_3††	3.53	3.53	3.65
$Fe_2O_3^s$	3.80	3.85	3.97	Fe_2O_3†	3.95	3.98	3.94
				Fe_2O_3††	3.86	3.91	3.91
CaO^{ss}	64.78	65.22	65.20	CaO*	64.87	64.85	64.88
MgO^s	2.08	2.19	2.18	MgO*	2.06	2.03	2.05
SO_3	1.92	1.97	1.93	SO_3†	1.90	2.05	1.86
Na_2O^s	0.09	0.21	0.15	Na_2O††	0.12	0.11	0.12
K_2O^s	0.49	0.47	0.51	K_2O††	0.47	0.46	0.51
TiO_2^s	0.19	0.18	0.18	TiO_2††	0.19	0.20	0.20
$P_2O_5^s$	0.14	0.16	0.12	$P_2O_5^s$	0.15	0.14	0.15
$Mn_2O_3^s$	0.017	0.019	0.013	Mn_2O_3††	0.01	0.01	0.01
BaO^s	0.03	0.05	0.04	BaO^s	0.03	0.03	0.03
SrO^s	0.07	0.07	0.07	SrO^s	0.07	0.06	0.06
LOI†	0.43	0.43	0.42	LOI†	0.36	0.32	0.35
TOTALS	100.18	100.89	100.84		100.19	99.97	100.13
<u>Other</u>							
CO_2	0.21	0.29	0.23			(not determined)	
Total Alkalies as Na_2O	0.41	0.52	0.49		0.43	0.41	0.46
Insoluble Residue		(not determined)			0.11	0.16	0.09

*Optional method

†Referee method

^{s}Emission Spectrometry

**Referee method, corrected for TiO_2 and P_2O_5

††Rapid method (AA); one standard reference material run with test samples

^{ss}EDTA

Table 13.2. Maximum Differences Among Three Samples, %.

	WES	Maximum Permissible Variable	PSU
SiO_3	0.04	0.24	0.10
Al_2O_3	0.03	0.10	0.11
Fe_2O_3	0.04	0.15	0.17
MgO	0.03	0.24	0.11
SO_3	0.19	0.15	0.05
LOI	0.04	0.15	0.01
CaO	0.03	0.30	0.44
Na_2O	0.01	0.05	0.12
K_2O	0.05	0.05	0.04
TiO_2	0.01	0.03	0.01
P_2O_5	0.01	0.05	0.04
Mn_2O_3	0.00	0.05	0.006
Insoluble residue	0.07	0.15	not determined

RC-853(2). The values given on Table 13.7 for calculated compound composition indicate that, in this respect, this cement complies with the relevant requirements of ASTM C 150 for Type V and API for Class H.

The calculated C_3A contents from the three PSU alumina values after correction for P_2O_5 and TiO_2 calculated to C_3A contents of 2.9, 2.8, and 2.4, so that PSU as well as WES found the class H HSR cement in compliance with the specifications for Type V in ASTM C 150 and API Class H HSR cement with respect to C_3A content.

13.2.4 Other Reference Comparisons (PSU)

The accuracy of PSU analyses is verified by analyses of the NBS standard reference materials (SRM). Also, two blended cements (#5 and #6 of the Blended Reference Sample Program) were analyzed on August 4, 1980. The results and the analyses from the CCRL Reference Samples Program (July 9, 1980) are compared in Table 13.8. All the PSU measured values are within the one standard deviation given by CCRL.

Table 13.3. Chemical Reference Sample Program Chemical Analysis Report Form,

TO:
H. G. Anderson, Jr.
Cement and Concrete Reference Laboratory
Room B-26, Technology Building
National Bureau of Standards
Washington, D. C. 20234

FROM: Structures Laboratory
USAE Waterways Exp Sta
ATTN: Cement & Pozzolan Group
P. O. Box 631
Vicksburg, MS 39180

DO NOT ENTER DATA ON THIS PAGE UNTIL YOU HAVE READ THE SPECIAL INSTRUCTIONS LISTED ON THE PINK PAGE PROCEDING THESE FORMS.

DATA REPORTED HERE SHOULD BE THAT OBTAINED FROM NORMAL PROCEDURES. IF ANY PROCEDURE, LISTED UNDER "OTHER" IS ONE OF THE "DRY METHODS", THEN THAT DATA SHOULD ALSO BE REPORTED ON THE BLUE SUPPLEMENTAL REPORT FORM. IF YOU DO A "DRY METHOD" IN ADDITION TO THE REPORTING METHOD, PLEASE, REPORT IT ON THE BLUE FORM ALSO.

REPORT VALUES TO NEAREST 0.01%

	Sample No.57	Sample No.58		ASTM Optional	ASTM Referee	Other
Silicon dioxide, SiO_2	20.52	19.79	(10)	X		
Aluminum oxide, Al_2O_3	6.52	5.98	(20)		X	
Ferric oxide, Fe_2O_3	2.56	2.52	(30)		X	
Calcium oxide, CaO	62.10	62.59	(40)	X		
Free lime	--	--	(41)	--	--	
Magnesium oxide, MgO	2.73	2.91	(50)	X		
Sulfur trioxide, SO_3	2.98	3.35	(60)		X	
Loss on ingnition	1.03	1.33	(70)		X	
Insoluble residue	0.30	0.26	(80)		X	
Sodium oxide, Na_2O	0.42	0.36	(90)		X	
Pottassium oxide, K_2O	1.11	1.06	(100)		X	

Remarks:

Tests made by: R. E. Richter

Reported by: W. G. MILLER
Date: 8/11/80

Table 13.4. Cement Reference Sample Program Physical Tests Report Form

TO:
H. G. Anderson
Cement and Concrete Reference Laboratory
Room B-26, Technology Building
National Bureau of Standards
Washington, D. C. 20234

FROM:
Structures Laboratory
USAE Waterways Exp Sta
ATTN: Cem & Pozz Group
P. O. Box 631
Vicksburg, MS 39180

	Sample No.57	Sample No.58	
NORMAL CONSISTENCY: Water, nearest 0.1 percent by weight of cement	26.6	25.6	(110)
VICAT TIME OF SETTING:	HRS.: MIN.	HRS.: MIN.	
Initial Set, Hrs.: Min. (nearest 5 min.) ...	2 : 30	1 : 55	(120)
Final Set, Hrs.: Min. (nearest 5 min.)......	4 : 30	4 : 10	(121)
GILLMORE TIME OF SETTING:			
Initial Set, Hrs.: Min. (nearest 5 min.)....	3 : 15	2 : 55	(130)
Final Set, Hrs.: Min. (nearest 5 min.)	5 : 15	4 : 35	(140)
FALSE SET (PASTE METHOD):			
Final Penetration/Initial Penetration, Nearest percent	72	79	(150)
AUTOCLAVE EXPANSION: Final Reading	1786	1882	
Initial Reading	1587	1781	
Difference	0199	0101	
Percent Expansion (nearest 0.01%)	0.20	0.10	(160)

Table 13.4 (Cont.)

		Sample No.57	Sample No. 58	
AIR ENTRAINMENT:	Nearest 0.1 percent	10.2	10.3	(170)
	Mixing Water, nearest 0.1 percent by weight of cement	67.4	67.4	(180)
	Flow obtained, nearest percent	80	80	(190)
COMPRESSIVE STRENGTH:	3-day, total load, lbs. (1) . . .	13080	15040	
	(2) . . .	13240	15640	
	(3) . . .	13000	15700	
	Avg. psi (nearest 10 psi)	3280	3860	(200)
	7-day, total load, lbs. (1) . . .	15500	17770	
	(2) . . .	15840	18140	
	(3) . . .	15790	17660	
	Avg. psi (nearest 10 psi)	3930	4460	(210)
FINENESS:	Air Permeability, cm^2/g (nearest 10 cm^2/g). .	3550	4080	(270)
FINENESS:	Wagner Turbidimeter, cm^2/g (nearest 10 cm^2/g)			(280)
FINENESS:	No. 325 Sieve, Corrected percent passing (nearest 0.01%)	93.48	93.44	(281)

Tests made by: ______________ Reported by: W. G. MILLER

Laboratory: WES Date: 8/14/80

Location: ______________

Table 13.4 (Cont.)

	Sample No. 57	Sample No. 58	
HEAT OF SOLUTION: Dry Cement, cal/g (nearest 0.1 cal/g)	604.9	605.0	(291)
Partially hydrated, 7-day cal/g (nearest 0.1 cal/g)	526.2	524.1	(292)
Partially hydrated, 28-day cal/g (nearest 0.1 cal/g)	SEE NOTE,	BELOW	(301)
HEAT OF HYDRATION:			
7-day, cal/g (nearest 0.1 cal/g)	78.8	81.1	(290)
28-day, cal/g (nearest 0.1 cal/g)	SEE NOTE,	BELOW	(300)

NOTE: Laboratories who perform these tests are requested to forward their 28-day results by separate letter.

Heat of Hydration calculations and diagrams are being forwarded only to those laboratories which return data for these tests unless a specific request is made. If you do not return data, but wish the information, please place an X in the box below:

☐

Tests made by: R. E. Richter
Laboratory: WES
Location:

Reported by: W. G. MILLER
Date: 8/11/80

Table 13.5

CCRL Reference Sample Program
Portland Cement Samples, Numbers 57 and 58
Preliminary Report, Chemical Results, September 12, 1980

Summary of Results

			Sample No. 57			Sample No. 58		
		NO OF LABS	Average	Stan Dev	C.V. 0/0	Average	Stan Dev	C.V. 0/0
Silica Oxide	PRCNT	49	2.0345+01	2.1719-01	1.068	1.9735+01	3.0699-01	1.556
Alum Oxide	PRCNT	49	6.4433+00	4.0249-01	6.247	6.0912+00	3.4580-01	5.677
Iron Oxide	PRCNT	49	2.6245+00	7.3947-01	2.818	2.5382+00	6.8825-02	2.712
Calc Oxide	PRCNT	48	6.2373+01	6.7825-01	1.087	6.2695+01	5.5364-01	.882
Free Lime	PRCNT	25	6.9560-01	2.5640-01	36.861	8.0800-01	2.1708-01	26.867
Magn Oxide	PRCNT	48	2.7425+00	1.6586-01	6.048	2.8744+00	1.9195-01	6.678
Sulf Trioxid	PRCNT	50	3.0010+00	1.3232-01	4.409	3.3774+00	1.1007-01	3.259
Loss on Ign	PRCNT	50	1.0116+00	1.1033-01	10.907	1.3356+00	1.4930-01	11.179
Insol Resid	PRCNT	45	2.0200-01	9.0418-02	44.762	2.2444-01	8.8306-02	39.344
Sodium Oxide	PRCNT	40	3.9025-01	1.2753.01	32.679	3.5225-01	1.4675-01	41.661
Potas Oxide	PRCNT	40	1.0365+00	1.7074.01	16.473	9.7750-01	1.5843-01	16.208

Table 13.6

CCRL Reference Sample Program
Portland Cement Samples. Numbers 57 and 58
Preliminary Report, Physical Results, September 12, 1980

Summary of Results

		No of Labs	Sample No. 57			Sample No. 58		
			Average	Stan Dev	C.V. 0/0	Average	Stan Dev	C.V. 0/0
N.C. Water	PRCNT	50	2.6660+01	4.4272-01	1.661	2.5674+01	4.3986-01	1.713
Vicat Ts Inl	MIN	46	1.4609+02	1.8796+01	12.865	1.1207+02	2.0209+01	18.034
Vicat Ts Fin	MIN	46	2.5391+02	5.1757+01	20.384	2.0511+02	5.1202+01	24.963
Gilmr Ts Inl	MIN	43	1.8256+02	3.4406+01	18.847	1.5035+02	2.6623+01	17.708
Gilmr Ts Fnl	MIN	43	3.1058+02	5.6021+01	18.037	2.6535+02	5.0948+01	19.200
False Set	PRCNT	30	6.8033+01	9.8872+00	14.533	5.3900+01	1.0213+01	18.948
Autocl Expan	PRCNT	47	2.3043-01	4.0160-02	17.429	1.2745-01	2.7144-02	21.299
Air Content	PRCNT	46	1.0100+01	1.9272+00	19.082	1.0241+01	1.8951+00	18.504
Ac Mix Water	PRCNT	44	6.9511+01	2.0908+00	3.008	6.8964+01	1.9719+00	2.859
Ac Flow	PRCNT	46	8.5870+01	3.1666+00	3.688	8.7783+01	3.4119+00	3.887
Comp Str 3D	PSI	50	3.2059+03	3.1422+02	9.801	3.8164+03	3.7473+02	9.819
Comp Str 7D	PSI	50	3.9160+03	3.5545+02	9.077	4.4804+03	3.8436+02	8.579
Fineness Ap	SQCM/G	48	3.4928+03	8.6297+01	2.471	4.1069+03	1.1656+02	2.838
Fineness Wt	SQCM/G	10	1.8800+03	7.3333+01	3.901	2.1630+03	1.5254+02	7.052
Pass 325 Sv	PRCNT	32	9.2890+01	2.2369+00	2.408	9.3045+01	1.2151+00	1.306

Table 13.7

TO Concrete & Grout Group Structures Laboratory WES	REPORT OF TESTS OF PORTLAND CEMENT RC-853-(2)	FROM: CORPS OF ENGINEERS U. S. ARMY Structures Laboratory USAE Waterways Exp Sta ATTN: Cem & Pozz Group P. O. Box 631 Vicksburg, MS 39180

TEST REPORT NO WES-305-80
BIN NO.
CWT REPRESENTED:
DATE: 15 July 80
SPECIFICATION: Class H
Revised 5 Oct 81
COMPANY Lone Star
LOCATION Maryneal, TX
BRAND:
THIS CEMENT DOES X MEET

	WET			INSTRUMENTAL				
SAMPLE NO.	1	2	3		1	2	3	METHOD
SiO_2, %	22.2	22.2	22.2	Al_2O_3	3.53	3.53	3.65	AA
Al_2O_3, % *	3.7	3.7	3.7					
Fe_2O_3, %	4.0	4.0	3.9	Fe_2O_3	3.86	3.91	3.91	AA
MgO, %	2.1	2.0	2.0	TiO_2	0.19	0.20	0.20	AA
SO_3, %	1.9	2.0	1.9					
LOSS ON IGNITION, %	0.4	0.3	0.4	P_2O_5	0.15	0.14	0.15	PE
ALKALIES-TOTAL AS Na_2O, %	0.43	0.41	0.46	Mn_2O_3	0.01	0.01	0.01	AA
Na_2O, %	0.12	0.11	0.12					
K_2O, %	0.47	0.46	0.51	BaO	0.03	0.03	0.03	PE
INSOLUBLE RESIDUE, %	0.11	0.16	0.09	SRO	0.07	0.06	0.06	PE
CaO, %	64.9	64.8	64.9	AA - Atomic Absorption				
C_3S, %	59	59	59	PE - Plasma Emission				
C_3A, %	3	3	3					
C_2S, %	19	20	19					
$C_3A + C_3S$, %	62	62	62					
C_4AF, %	12	12	12					
$C_4AF + 2 C_3A$, %	18	18	18					
% passing 45μm (no 325) sieve	66.0	65.0	62.0					
SURFACE AREA, m^2/Kg	230	237	235					
AIR CONTENT, %	10.2	10.2	10.0					
COMP. STRENGTH, 3 D, PSI	1670	1580	1500					
COMP. STRENGTH, 7 D, PSI	2360	2140	2160					
COMP. STRENGTH **28 D, PSI	3300	3280	3260	90 day	4090	4120	4190	
Density, Mg/m^3	3.19	3.19	3.17					
SAMPLE NO.	1	2	3					
AUTOCLAVE EXP., %	0.00	0.00	0.00					
INITIAL SET, HR/MIN	4:20	4:20	4:20					
FINAL SET, HR/MIN	6:20	6:20	6:20					
SAMPLE NO.								
AUTOCLAVE EXP., %								
INITIAL SET, HR/MIN								
FINAL SET, HR/MIN								

REMARKS Memo for all concerned #2096 **28 day test results
CC: Job # 441-S866.10SC51

*Referee Al_2O_3 corrected for TiO_2 + P_2O_5

Revised 10/5/81 to exclude TiO_2 and P_2O_5 from calculated compounds.

THE INFORMATION GIVEN IN THIS REPORT SHALL NOT BE USED IN ADVERTISING OR SALES PROMOTION TO INDICATE EITHER EXPLICITLY OR IMPLICITLY ENDORSEMENT OF THIS PRODUCT BY THE U. S. GOVERNMENT.

W. G. MILLER
Chemist
Chief, Cement & Pozzolan Group

ENG FORM 1 MAR 71 6008-R

Table 13.8. Comparison of Analyses (PSU) with CCRL Reference Sample Blended Cements Analyses, %.

	NBS B-5				NBS B-6			
	CCRL Report				CCRL Report			
	PSU	Mean $\bar{x}$	σ	(PSU-$\bar{x}$)	PSU	Mean $\bar{x}$	σ	(PSU-$\bar{x}$)
SiO_2	27.9	27.33	2.34	0.57	26.4	26.2	2.50	0.2
Al_2O_3	9.00	9.22	2.09	-0.22	7.40	8.04	1.83	-0.64
MgO	2.70	2.777	0.43	-0.08	3.46	3.449	0.47	0.151
CaO	52.26	53.56	1.30	-1.30	53.79	54.42	1.36	-0.63
SO_3	2.03	2.171	0.31	-0.14	2.26	2.36	0.30	-0.10
LOI	2.07	1.86	0.24	0.21	1.22	1.17	0.13	0.05

13.2.5 Interlaboratory Comparison

The agreement between the results of the measurements in the two laboratories on the Class H cement is good for the determinations made by both, as shown in Table 13.9. Values for each component of the chemical analyses (Table 13.9) show in all cases that the differences are less than the maximum permissible variation allowed in Table 1 of ASTM C 114 if the analyses were considered two test results in the same laboratory.

Similar observations have been made for the fly ash, as shown in Table 13.10. On the whole the determinations made in both laboratories are tightly grouped. Major oxide differences range from 0.01% for CaO, 0.5% for SiO_2 and MgO to 0.9% for Al_2O_3. Minor components range from about 0.05 for Na_2O and 0.13% for SO_3, to larger values for P_2O_5 and TiO_2; and 0.04% for LOI. Fly ashes are characteristically nonhomogeneous, and the differences observed are comparable to those expected from individual measurements on fly ash from the same source, within a single laboratory.

13.2.6 Conclusions

The magnitude of interlaboratory variation is comparable to the kinds of variation seen in various interlaboratory chemical analyses of cements. The interlaboratory variation in the fly ash analyses is comparable to that found on measurements of a single source of fly ash within a single laboratory.

Table 13.9. Interlaboratory Variation in Chemical Analytical Data for Class H Cement, %

	PSU, $\bar{x}_p$	WES, $\bar{x}_w$	$\bar{x}_p - \bar{x}_w$
SiO_2	22.27	22.23	0.04
Al_2O_3	3.82	3.72	0.10
Fe_2O_3	3.87	3.96	-0.09
CaO	65.07	64.87	0.20
MgO	2.15	2.07	0.08
SO_3	1.94	1.93	0.01
Na_2O	0.15	0.12	0.03
K_2O	0.49	0.48	0.01
TiO_2	0.18	0.20	-0.02
P_2O_5	0.14	0.15	-0.01
Mn_2O_3	0.02	0.01	0.01
BaO	0.04	0.03	0.01
SrO	0.07	0.06	0.01
LOI	0.43	0.37	0.06
Total Alkalies as Na_2O	0.47	0.43	0.03

Table 13.10. Chemical Analyses of Fly Ash, %.

	PSU # B26	WES # AD-592 (4)
Component		
SiO_2	33.2	32.7
Al_2O_3	17.6	16.7
Fe_2O_3	6.03	6.4
CaO	29.91	29.9
MgO	5.07	5.6
SO_3	2.77	2.9
Na_2O	1.03	0.98
K_2O	0.41	0.36
TiO_2	1.55	1.58
P_2O_5	0.95	1.04
Mn_2O_3	0.08	0.04
BaO	0.84	0.69
SrO	0.37	0.34
LOI	0.44	0.4
Moisture content	0.06	0.1
TOTALS	100.31	99.73
Other		
CO_2	0.22	not determined
Total Alkalies as Na_2O	1.30	1.22

13.3 Density by LeChatelier Flask

Density determinations of the Class H cement and fly ash samples were made by both laboratories using a LeChatelier flask and the procedure set forth in C 188. Results are given in Table 13.11.

13.3.1 Comparison of Measurements

The single operator standard deviation for portland cements has been found to be 0.012. PSU found a standard deviation of 0.013 on four determinations; WES found a standard deviation of 0.012 on three measurements. No precision statement for density of fly ashes has been published. The maximum difference between single determinations of density of fly ash by PSU and WES was 0.082; the maximum difference between single determinations of density of the Class H cement was 0.03, which is well within the allowable difference (2DS limits) for two properly conducted tests from two different laboratories on samples of the same cement.

Table 13.11. Density Determinations for Class H Cement and Fly Ash

Class H Cement, g/cc			
PSU # H7		WES # RC-853(2)	
Density	3.16	Density	3.19
	3.19		3.19
	3.17		3.17
	3.18	Mean $\bar{x}$ =	3.183
Mean $\bar{x}$ =	3.175	σ' =	0.012
σ' =	0.013	V% =	0.38
V% =	0.40		
Fly Ash, g/cc			
PSU # B26		WES # AD-592(4)	
Density	2.628	Density	2.70
	2.634		2.70
	2.638		2.70
	2.650		2.71
Mean $\bar{x}$ =	2.640	Mean $\bar{x}$ =	2.703
σ' =	0.008	σ' =	0.006
V% =	0.30	V% =	0.21

13.4 Density by 25 mL Pycnometer (PSU)

As an additional check on density determined by LeChatelier Flask, density was also measured with a 25 mL pycnometer and water-clear kerosene according to general procedures given in ASTM C 329. The values obtained for the Class H cement and the fly ash were 3.18 g/cc* and 2.65 g/cc, respectively. These values are in good agreement with values for cement determined by both laboratories as described in Section 13.3.1, and with values for fly ash determined at PSU.

13.5 Fineness by Air-Permeability Method

13.5.1. Surface area measurements of the Class H cement and the fly ash were made by both laboratories using the air-permeability ("Blaine") method as described in ASTM C 204. In each case a standard sample of cement (NBS Standard Reference Material No. 114-m) was run with the unknowns in order to calibrate the apparatus.

Results for both laboratories are given in Table 13.12.

13.5.2 Comparison of Measurements

Precision of measurements on an intralaboratory basis is adequate. Within-laboratory coefficients of variation for three tests were within the allowable 3.4% of the average for two tests. The between-laboratory difference on two similar, but not identical, samples was 3.4%; 6.0% is allowable for "identical samples of the same material." No precision statement for surface area by the air permeability method of fly ash has been published. While the difference between the mean of three determinations of surface area of Class H cement made at PSU and three made at SL, WES, was approximately 100 cm^2/g, the difference in mean surface area of fly ash of three determinations made at PSU and one made at SL, WES was 740 cm^2/g. A difference of 100 cm^2/g in surface area between two lots of one type of cement from one plant is negligible while a difference of 740 cm^2/g is regarded as indicating a real change. If the surface areas of the fly ash as reported by the two laboratories are each multiplied by the density reported by the same laboratory, the surface area in cm^2/cc is 8940 for PSU and 11,160 for SL, WES—a difference of 2220 cm^2/cc, more than 20% of the PSU value and more than 15% of the WES value. Probably the fly

Table 13.12. Air-Permeability Surface Area, cm^2/g

	Class H			Fly Ash	
	PSU # H-7	WES # RC-853(2)		PSU # B26	WES # AD-592(4)
	2420	2330		3384	4,130
	2410	2290		3377	
	2430	2380		3403	
Mean $\bar{x}$ =	2420	2333	Mean $\bar{x}$ =	3388	
σ' =	10	45	σ' =	13.4	
V% =	0.41	1.9	V% =	0.40	

ash shipped by WES to PSU segregated to some degree in shipment and was not adequately re-blended before the measurements of density and surface area were made. It appears that the coarse light particles rose to the upper part of the container, so that the samples for density yielded lower results and the samples for surface area yielded coarser results than those found at WES. This hypothesis is supported by the observation that the fourth fly ash density measured at WES, on a sample retained from the shipment to PSU, was 2.71 g/cc.

13.6 Fineness by Wet Sieving

13.6.1 PSU — Wet sieving determinations were made for both the Class H cement (H-7) and the fly ash (B26). The determinations used a 45-μm (No. 325) sieve according to ASTM 430.

13.6.2 WES — Wet sieve analyses were made on the fly ash [AD-592(4)] and on the Class H cement according to ASTM C 430.

13.6.3 Results and Comparison of Meausrements — Results for both laboratories are given in Table 13.13. The fly ash values obtained are within 1.2% of each other. The multilaboratory precision for tests on a high fineness cement (i.e. a cement of fineness more like the fly ash tested in this program than a low fineness cement would be) has been found to be ±0.50% (1S). Results of properly conducted tests from two different laboratories should agree 95% of the time within ±1.4% on identical samples of cement. No comparable precision statement exists for fly ash but the two results differ by only 1.2%. The Class H cement is a coarse cement; results at the two laboratories differed by 2.2%. For a cement of normal fineness, results of properly conducted tests from two different laboratories on identical samples should agree 95% of the time within ±2.1%. There is no discussion of precision of tests on low fineness products.

Table 13.13. Fineness by Wet Sieving.

45 µm (No. 325) Sieve		45 µm (No. 325) Sieve	
Class H Residue, % Retained		Fly Ash Residue, % Retained	
PSU (H-7)	WES [RC-853(2)]	PSU (B26)	WES [AD-592(4)]
33.5	35.7	14.8	16

13.7 Other Physical Tests of Cement (WES)

In normal cement quality control during manufacture and during acceptance testing of cement for use in concrete or other purposes, cements are required to be tested for air content in mortar, compressive strength at selected ages (using 2-in. [50.8-mm] cube specimens), soundness by autoclave expansion, and for time of setting. Cement RC-853(2) was so tested at SL and the results are given in Table 13.14.

13.8 Other Data on Fly Ash (WES)

WES report 126C-80 is attached as Table 13.15. On it are given all the data developed at SL in the normal process of characterizing such a material by routine physical and chemical methods as needed for acceptance for use in construction.

Table 13.14. Physical Tests on RC-853(2) Cement.

	(1)	(2)	(3)	Mean	σ'	V,%
Air content, %[†]	10.2	10.2	10.2	10.13	0.115	1.14
Compressive Strength[††] of 2-in. (50.8-mm) cubes, psi				Maximum Difference in Coefficient of Variation		
				Found	Within Lab	
3 days	1670	1580	1500	10.7 %	10.7%	
7 days	2360	2140	2160	9.78%	10.7%	
28 days	3300	3280	3260	1.22%	10.7%	
Autoclave Expansion, %:(S)	0.00	0.00	0.00	0.00%		
Initial Setting Time, hr, min:(SS)	4.20	4.20	4.20	0.00	No precision statement in this method	
Final Setting Time, hr, min:	6.20	6.20	6.20	0.00		

[†] ASTM Designation C 185, Standard Test Method for Air Content of Hydraulic Cement Mortar.

[††] ASTM Designation C 109, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars; single laboratory differences between batches of mortar made on the same day or within the week, applied to three batches.

(S) Expansion is below the range for which the precision statement of ASTM Designation C 151 (Standard Test Method for Autoclave Expansion of Portland Cement) has been written.

(SS) ASTM Designation C 266, Standard Test Method for Time of Setting of Hydraulic Cement by Gillmore Needles.

Table 13.15.

LABORATORY:		REPORT NO.:
Structures Laboratory USAE Waterways Exp St ATTN: Cem & Pozz Group P.O.Box 631 Vicksburg, MS 39180	REPORT OF TESTS ON POZZOLAN SS-C-1960/5 AD-592(4)	WES-126C-80 SHEET 1 OF 1 DATE: 2 April 80 25 April 80

CLASS F N(C) KIND OF POZZOLAN: Fly Ash (Litepoz III)

SOURCE: Southwest Public Serv, Amarillo, TX BRAND:

TEST RESULTS OF THIS SAMPLE LOT ☐ COMPLY ☐ DO NOT COMPLY WITH SPECIFICATION LIMITS (SEE REMARKS)

FOR USE AT: Wipp Project

CONTRACT NO.:

DISTRICT(S):

SAMPLED BY: Concrete & Grouting DATE SAMPLED: 13 Feb 80

CAR NO.: BIN NO.:

FIELD SAMPLE NO.: LAB SAMPLE NO.:

DATE RECEIVED: 24 March 80 LAB JOB NO.:

TESTED BY: Cem & Pozz Group CHECKED BY:

TESTS ON COMPOSITE OF THE 100-TON SAMPLES LISTED BELOW

$SiO_2 + Al_2O_3 + Fe_2O_3$ %	MgO %	SO_3 %	AVAILABLE ALKALIES %	POZZOLAN STRENGTH % CONTROL	INCREASE IN SHRINKAGE % (a)	AUTOCLAVE EXPANSION	REDUCTION IN EXPANSION % (b)
REQUIREMENTS							
MIN 70.0	MAX 5.0	MAX 4.0	MAX 1.50	MIN 75	MAX 0.03	MAX 0.50	MIN 75
TEST RESULTS							
58.5	5.6	2.9	* 1.22	* 131		0.08	

TESTS ON SAMPLES REPRESENTING 100 TONS OR LESS

SAMPLE NO.	MOISTURE CONTENT %	LOSS ON IGNITION %	Fineness 325 Mesh Sieve % Retained	% pts var from avg prev 10	LIME POZZOLAN STRENGTH PSI	WATER REQUIREMENT % of Control	SPECIFIC GRAVITY	SP GR VARIATION FROM AVERAGE OF PRECEDING 10, %
REQUIREMENTS								
—	MAX 3.0	MAX 10.0 (N) 6.0 (F)	MAX 34	MAX 5	MIN 900	MAX 105	—	MAX 5
TEST RESULTS								
1	0.1	0.4	16		880	89	2.70	
SiO2	32.7%		Total Alkalies			BaO	0.69	PE
** Al203	16.7%		Na20		0.98%	SRO	0.34	PE
** Fe203	6.4%		K20		0.36%	TIO_2	1.04	PE
CaO	29.9%		Total as Na20		1.22%	P_2O_5	~~1.55~~	~~PE~~
**	A-A analysis.							
FINENESS - 11,140 Sq			cm/cc			Mn_2O_3	0.04	AA
	4,130 Sq		cm/g.					
AVERAGE	—	—		—	—	—		—

(a) APPLICABLE ONLY TO CLASS N

(b) OPTIONAL REQUIREMENT

LABORATORY CEMENT USED Class II, WES-125-80

LABORATORY LIME USED Chemstone

REMARKS: Job #441-S859.20SC21 *28 day test results.

W. G. Miller

W. G. MILLER
Chemist
Chief, Cement & Pozzolan Group

NOTE: THE INFORMATION GIVEN IN THIS REPORT SHALL NOT BE USED IN ADVERTISING OR SALES PROMOTION TO INDICATE EITHER EXPLICITLY OR IMPLICITLY ENDORSEMENT OF THIS PRODUCT BY THE U. S. GOVERNMENT.

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13.9 X-ray Diffraction Data for Cement and Fly Ash

13.9.1 Introduction

Both laboratories ran x-ray diffraction scans using their respective instruments and calibration procedures and have reported their d-spacings and associated peak intensities. The data are best reported as a series of tables in which precision is addressed by tabulating differences between measurements made by both laboratories for both d-spacings and relative intensities. The data for the cement and the fly ash are presented in Tables 13.16 and 13.17, respectively. Intensities measured at WES were on a logarithmic scale.

13.9.2 Results

The spread of observed d-spacings for the Class H cement and fly ash samples studied by both laboratories ranged from 0.04 to 0.00 Angstroms* for low angle peaks and from 0.009 to 0.000 Angstroms for high-angle peaks. Intensity differences ranged from 36 to 0 percent. Agreement between laboratories was good considering that each laboratory used a different x-ray diffractometer and different sample mounting and standardization procedures. The data in Tables 13.16 and 13.17 and additional peaks in the actual charts indicated the following compositions for these materials:

a. Cement RC-853(2). This had a normal cement composition of alite and belite with lesser amounts of calcium aluminoferrite, calcium sulfate, and possibly MgO. A small amount of tricalcium aluminate (C_3A) was tentatively identified in the as-received cement and verified as being non-cubic C_3A in the residue after maleic acid treatment.

b. Fly Ash AD-592(4). The crystalline phases were identified as the quartz, mullite, hematite, and magnetite found in most fly ashes, along with lime (CaO), periclase (MgO), calcium sulfate, tetracalcium trialuminate sulfate, calcite, a calcium aluminoferrite solid solution, and possibly metallic iron. The phases other than the first four listed are some of those that may be found in fly ash such as this from lignite or sub-bituminous coal.

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*Angstrom x 1.000,000 E-10 = meter. Although the Angstrom (A) is not an SI unit, it is used here because all of the reference spacings are in Angstroms.

Table 13.16. X-ray Diffraction Data: d-spacings and intensities of Class H cement.

a. PSU #H-7		b. WES RC-853 (2)			d-spacing spread, A††	relative intensity (I) spread††, a-b
d	I	d*	c/s**	I†	a-b	
7.30	2	7.31	13	5	0.01	3
5.94	3	5.98	12	4	0.04	1
		5.50	4	1	---	--
3.87	6	3.864	11	4	0.006	2
3.66	1	3.66	6	2	0.00	1
3.53	3	3.531	8	3	0.001	0
		3.477	4	1	---	--
3.30	1	3.393	2	1	0.003	0
		3.245	4	1	---	--
3.10	3	3.195	6	2	0.005	1
3.030	55	3.035	190	69	0.005	14
2.965	15	2.966	32	12	0.001	3
2.882	4	2.873	6	2	0.009	2
2.773	100	2.778	274	99	0.005	1
2.743	78	2.744	277	100	0.001	22
2.692	11	2.693	24	9	0.001	2
2.650	21	2.657	32	12	0.007	9
2.605	76	2.612	265	96	0.007	20
		2.494	2	1	---	--
2.443	12	2.447	16	6	0.004	6
2.41	3				---	--
2.377	1				---	--
2.319	18	2.319	21	8	0.00	10
2.285	4	2.291	7	3	0.006	1
1.183	45	2.184	113	41	0.001	4
1.163	12	2.169	24	9	0.006	3
2.14	5				---	--
2.105	4	2.102	5	2	0.003	2
2.088	5				---	--
2.055	12	2.061	10	4	0.006	2
2.037	22	2.034	5	2	0.003	20
1.988	8				---	--
1.978	10	1.979	14	5	0.001	5
1.931	16	1.932	25	9	0.001	8
1.916	8				---	--
		1.850	9	3	---	--
1.823	10	1.833	13	5	---	--
1.766	43	1.827	11	4	0.004	5
1.760	40	1.763	158	57	0.003	7
		1.726	3	1	---	--
1.689	4	1.694	7	3	0.005	1
1.640	3	1.641	7	3	0.001	0
1.625	33	1.625	33	12	0.00	21
1.574	5	1.576	7	3	0.002	2
1.540	18	1.538	28	10	0.002	8

Table 13.16 (continued)

a. PSU #H-7		b. WES RC-853 (2)			d-spacing spread, A[††] a-b	relative intensity (I) spread[††], a-b
d	I	d*	c/s**	I[†]		
1.523	4	1.524	8	3	0.001	1
1.488	36	1.487	42	15	0.001	21
		1.473	7	3	---	--
1.462	5				---	--
1.4587	9	1.4617	12	4	0.0013	5
1.452	5				---	--
1.434	3	1.430	5	2	0.004	1
1.431	4				---	--
1.402	3				---	--
1.3865	9				---	--
1.382	7				---	--

*The 0.2 2θ/min scale was used to determine d-spacings.

**Calculated using rate meter calibration charts for the XRD-700.

[†] Intensity converted from c/s to percentage of the maximum intensity for the WES pattern scanned at 0.2° 2θ/min, d = 2.744, I = 277 c/s.

[††] Absolute values.

Table 13.17. X-ray Diffraction Data: d-spacings and intensities of fly ash.

a. PSU #B-26		b. WES AD-592 (4)			d-spacing spread, A† a-b	relative intensity (I) spread,† a-b
d	I	d*	c/s**	I		
		7.31	7	2		
4.26	17	4.26	83	23	0.00	6
4.07	2				--	--
3.748	17	3.751	62	17	0.01	12
3.497	32	3.504	104	29	0.00	2
3.348	100	3.348	359	100	0.00	0
		3.173	16	5	--	--
3.034	12	3.035	16	5	0.001	7
2.967	10	2.966	16	5	0.001	5
2.855	26	2.855	44	12	0.00	14
2.767	41	2.769	143	40	0.002	1
2.740	28				---	--
2.690	5	2.688	254	71	0.002	14
		2.650	52	15	---	--
2.600	23	2.605	24	7	0.005	1
2.534	13	2.533	24	7	0.001	6
2.461	13	2.466	16	5	0.005	8
		2.449	24	7	---	--
2.431	9	2.434	16	5	0.003	4
2.397	83	2.396	256	71	0.001	12
2.330	5	2.336	16	5	0.006	0
		2.328	16	5	---	--
2.288	11	2.291	32	10	0.003	1
2.239	6				--	--
2.209	18	2.205	40	11	0.004	7
		2.184	32	9	---	--
2.132	7	2.130	28	8	0.002	1
2.108	72	2.106	128	36	0.002	36
2.061	5				---	--
1.982	3	1.984	16	5	0.002	2
1.945	4	1.947	24	7	0.002	3
		1.932	24	7	---	--
1.901	21	1.901	54	15	0.00	7
1.871	4	1.868	16	5	0.003	1
1.821	19	1.823	38	11	0.002	8
1.763	4	1.762	13	7	0.001	3
1.758	8	1.751	16	5	0.007	3
1.695	47	1.697	98	27	0.002	20
1.674	3				---	--
		1.627	16	5	---	--
1.619	4	1.614	36	10	0.005	6
1.552	23	1.551	56	16	0.001	7
1.542	19				---	--
1.524	8	1.527	16	5	0.003	3
1.490	45	1.489	70	19	0.001	26
1.486	27	1.483	16	5	0.003	22
1.445	10	1.446	30	8	0.001	2
1.384	21	1.386	36	10	0.002	11
1.374	11	1.379	30	8	0.005	3

*The 0.2° 2θ/min scan was used to determine d-spacing.

**Approximate calculation using rate meter calibration charts for XRD-700. Rate meter was used at 15 units offset in preparing the calibration chart while the x-ray pattern run was 20 units offset.

†Absolute values.

14.0 Characterization of Cement Paste and Grout

14.1 Early Heat of Hydration of Cement and Grout (PSU)

Comparisons were made between the hydration behavior of the Class H cement alone and the total mixture formulations. Differential data are reported, which indicate rates of hydration. Two thermal peaks were recorded during the 45-hr duration of the three calorimeter experiments. The instantaneous peak, which is due to the adsorption of water and the initial heat of reaction of tricalcium aluminate, was separated from the second peak by the induction period during which no heat was evolved. The accelerated period (or second thermal peak) which occurs after the induction period is characteristic of C_3S hydration. This peak began to develop at 11 hr, and peaked at approximately 22 hr after mixing. In comparison, the second peak for Class H cement with deionized water at 25°C began to develop at 2 hr. and peaked approximately 8 hr after mixing, but was less intense. Heats of hydration for both mixtures are given in Table 14.1.

Table 14.1. Early Heat of Hydration

	Maximum Rate of Hydration, cal/g-hr		2nd Peak	
	1st peak	2nd peak	Starting Time, hr	Peak Position, hr
PSU/WES formulation at 38°C	11.2	1.37	11	22
Class H + deionized water at 25°C	----	0.66	2	8

14.2 X-ray Diffraction Data for Hydrated Cement Grout

Samples of hydrated grout were subjected to x-ray diffraction analysis as described in Section 9.0. As was the case in presenting x-ray data for the starting materials (Class H cement and fly ash, Section 13.9), these data are presented in tabular form, listing d-spacings and intensities for similarly hydrated grouts independently run by each laboratory. A comparison of the PSU and WES data for sealed vial-cured samples x-rayed in the "as-cured condition"* for 3, 7, 28, 56, 90, 180 (or 181), and 365 days of hydration are presented as a series of Tables (14.2 through 14.8). These tables show peaks generally seen by both laboratories and are intended for comparison of peak positions as measured by the two laboratories. The same is true for the x-ray data in Tables 13.16 and 13.17. However, phase identifications at WES and PSU which are discussed later in the text were based on the actual x-ray diffraction patterns which included more peaks. Representative patterns are illustrated by Figures 14.1 and 14.2, which are copies of the 181 and 180 day x-ray diffraction patterns of WES and PSU, respectively.

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*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

Table 14.2. X-ray Diffraction Data: d-spacings and relative intensities of 3-day "as-cured"* sealed vial samples.

PSU		WES			d-spacing spread	relative intensity (I) spread
d	I	d	c/s**	I	A	
9.64	20	9.73	142	†	0.09	--
5.91	6	5.94	6	†	0.03	--
5.58	24	5.61	83	20	0.03	4
4.90	13	4.93	239	59	0.03	46
4.70	12	4.72	54	13	0.02	1
3.87	31	3.89	96	24	0.02	7
		3.66	18	5	--	--
3.59	7	3.61	24	6	0.02	1
3.46	19	3.48	36	9	0.02	10
3.34	20	3.35	48	12	0.01	8
3.23	6	3.25	27	7	0.02	1
3.03	80	3.04	90	22	0.01	58
2.958	20	2.974	42	10	0.016	10
2.882		2.882	33	8	0.000	--
2.874	10				---	--
2.770	100	2.774	404	100	0.004	0
2.737	87	2.746	155	38	0.009	49
2.626	83	2.633	319	79	0.007	4
2.602	82	2.606	164	41	0.004	41
2.561	34	2.563	60	15	0.002	19
2.438	9	2.440	18	4	0.002	5
2.316	10	2.319	30	7	0.003	3
2.281	13	2.286	30	7	0.005	6
2.206	43	2.208	78	19	0.002	24
2.179	36	2.181	81	20	0.002	16
2.151	24	2.155	42	10	0.004	14
2.104	17	2.106	30	7	0.002	10
1.975	14	1.980	18	5	0.005	9
1.928	53	1.929	148	37	0.001	16
1.797	39	1.797	85	21	0.000	18
1.764	49	1.763	160	40	0.001	9
1.758	39				---	--
1.687	20	1.687	54	13	0.000	7
1.662	12	1.665	22	5	0.003	7
1.621	17	1.622	20	5	0.001	12
1.539	24	1.540	24	6	0.001	18
1.535		1.527	7	2	0.008	--
1.489	24				---	--
1.483	26	1.485	58	14	0.002	12

*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

**Based on XRD-700 ratemeter calibration charts.

†Run at different power so not feasible to be included.

Table 14.3. X-ray Diffraction Data: d-spacings and relative intensities of 7-day "as-cured"* sealed vial samples.

PSU		WES			d-spacing spread A	relative intensity (I) spread
d	I	d	c/s**	I		
9.72	22	9.71	208	†	0.01	--
5.61	29	5.60	116	27	0.01	2
4.92	20	4.92	258	60	0.00	40
4.69	18	4.72	64	15	0.03	3
4.26	4	4.27	18	4	0.01	0
3.88	35	3.88	111	26	0.00	9
		3.66	18	4	--	--
3.47	8	3.48	42	10	0.01	2
3.34	32	3.35	170	39	0.01	7
3.23	13	3.23	30	7	0.00	6
3.11	20	3.11	80	19	0.00	1
3.03	49	3.02	72	17	0.01	32
2.961	10	2.966	26	6	0.005	4
2.772	100	2.769	223	52	0.003	48
2.746	66				---	--
2.734	70	2.736	152	35	0.002	35
2.629	83	2.627	431	100	0.002	17
2.602	59	2.605	84	19	0.003	40
2.562	35	2.562	64	15	0.000	20
2.403	13	2.402	30	8	0.001	5
2.206	49	2.205	97	23	0.001	26
2.179	37	2.179	97	23	0.000	14
2.151	27	2.154	54	13	0.003	14
2.104	9	2.106	36	8	0.002	1
2.057	21	2.056	30	8	0.001	13
1.928	56	1.928	136	32	0.000	24
1.816	22	1.823	44	10	0.007	12
1.796	59	1.796	98	23	0.000	36
1.764	50	1.763	60	14	0.001	36
1.758	37				---	--
1.686	25	1.688	56	13	0.002	12
1.663	17	1.662	14	3	0.001	14
1.623	20				---	--
1.574	11	1.576	20	5	0.002	6
1.540	10	1.538	33	8	0.002	2
1.489	34	1.489	77	18	0.000	16
1.484	43	1.485	89	21	0.001	22
1.448	10	1.450	30	7	0.002	3

*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

**Based on XRD-700 ratemeter calibration charts.

†Run at different power so not feasible to be included.

Table 14.4. X-ray Diffraction Data: d-spacings and relative intensities of 28-day "as-cured"* sealed vial samples.

PSU		WES			d-spacing spread	relative intensity (I) spread
d	I	d	c/s**	I	A	
9.71	19	9.75	22	†	0.04	—
5.60	15	5.61	55	17	0.01	2
4.97	8				--	--
4.91	9	4.92	248	78	0.01	69
4.69	10	4.71	44	14	0.02	4
3.87	24	3.87	68	21	0.00	3
		3.66	21	7	--	--
3.60	5	3.59	24	8	0.01	3
3.47	12	3.47	38	12	0.00	0
3.34	14	3.34	103	32	0.00	18
3.24	10	3.24	44	14	0.00	4
3.03	100	3.03	103	32	0.00	68
2.881	18	2.882	80	25	0.001	7
2.773	51	2.771	202	64	0.002	13
2.741	63	2.744	163	51	0.003	12
2.627	49	2.629	317	100	0.002	51
2.599	30	2.608	129	41	0.009	11
2.562	27	2.563	72	23	0.001	4
2.496	12				---	--
2.405	9	2.405	22	7	0.000	2
2.285	16	2.285	18	6	0.000	10
2.206	26	2.207	57	18	0.001	8
2.181	15	2.181	77	24	0.000	9
2.150	11	2.159	37	12	0.009	1
2.096	17	2.106	30	9	0.010	8
2.053	15	2.055	28	9	0.002	6
1.943	6				---	--
1.927	31	1.928	114	36	0.001	5
1.909	22				---	--
1.874	16				---	--
1.821	17	1.821	36	11	0.000	6
1.796	24	1.795	86	27	0.001	3
1.764	30	1.763	32	10	0.001	20
1.759	36				---	--
1.686	18	1.686	43	14	0.000	4
1.662	15	1.662	24	8	0.000	7
1.539	4	1.540	13	4	0.001	0
1.529					---	--
1.489	15				---	--
1.482	13	1.483	46	14	0.001	1

*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

**Based on XRD-700 ratemeter calibration charts.

†Run at different power so not feasible to be included.

Table 14.5. X-ray Diffraction Data: d-spacings and relative intensities of 56-day "as-cured"* sealed vial samples.

PSU		WES			d-spacing spread	relative intensity (I) spread
d	I	d	c/s**	I	A	
9.61	24	9.75	141	†	0.14	--
7.23	7	7.31	19	†	0.08	--
5.57	21	5.60	122	35	0.03	14
4.89	29	4.91	205	59	0.02	30
4.67	15	4.69	66	19	0.02	4
3.86	36	3.87	120	35	0.01	1
		3.65	24	7	--	--
3.59	9	3.60	33	10	0.01	1
3.48	32	3.47	59	17	0.01	15
3.33	46	3.34	173	50	0.01	4
3.22	15	3.23	58	17	0.01	2
3.10	27	3.11	94	27	0.01	0
3.02	43	3.02	109	32	0.00	11
2.870	29	2.875	78	23	0.005	6
2.767	79	2.769	245	71	0.002	8
2.731	76	2.738	133	38	0.007	38
2.621	100	2.624	345	100	0.003	0
2.598	74	2.602	104	30	0.004	44
2.556	37	2.562	104	30	0.006	7
2.402	12	2.404	36	10	0.002	2
2.313	11	2.316	32	9	0.003	2
2.278	13	2.283	29	8	0.005	5
2.204	42	2.204	92	27	0.000	15
2.176	24	2.178	103	30	0.002	6
2.148	25	2.151	69	20	0.003	5
2.101	14	2.102	42	12	0.001	2
2.053	14	2.053	42	12	0.000	2
1.924	65	1.925	117	34	0.001	31
1.793	61	1.794	77	22	0.001	39
1.762	38	1.759	41	12	0.003	26
1.684	29	1.685	40	12	0.001	17
1.660	23	1.663	34	10	0.003	13
1.622	29	1.620	25	7	0.002	22
1.572	26	1.574	28	8	0.002	18
1.488	32	1.489	37	11	0.001	21
1.481	44	1.483	44	13	0.002	31
1.447	23	1.448	24	7	0.008	16
1.313	10	†			--	--

*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

**Based on XRD-700 ratemeter calibration charts.

†Run at different power so not feasible to be included.

Table 14.6. X-ray Diffraction Data: d-spacings and relative intensities of 90-day "as-cured"* sealed vial samples.

PSU		WES			d-spacing spread	relative intensity (I) spread
d	I	d	c/s**	I	A	
9.61	27	9.73	142	†	0.12	--
5.57	25	5.61	75	24	0.04	1
4.88	35	4.92	210	68	0.04	33
4.67	23	4.72	39	12	0.05	11
3.86	38	3.88	64	21	0.02	17
		3.66	10	3	---	--
3.45	3	3.48	37	12	0.03	9
3.33	19	3.35	82	26	0.02	7
3.22	7	3.24	40	13	0.02	6
3.10	12	3.12	95	31	0.02	19
3.01	27	3.02	140	45	0.01	18
2.768	59	2.774	205	66	0.006	7
2.731	54	2.741	105	34	0.010	20
2.622	100	2.629	310	100	0.007	0
2.554	32	2.560	71	23	0.006	9
2.309	3	2.319	20	7	0.010	4
2.277	8	2.278	17	6	0.001	2
2.200	30	2.208	55	18	0.008	12
2.175	24	2.177	73	24	0.002	0
2.147	17	2.149	35	11	0.002	6
2.097	21	2.102	20	6	0.005	15
2.050	21	2.047	25	8	0.003	13
1.924	44	1.924	158	51	0.000	7
1.822	19	1.819	40	13	0.003	6
1.792	47	1.791	93	30	0.002	17
1.759	18	1.753	28	9	0.006	9
1.682	17	1.682	51	16	0.000	1
1.658	11	1.660	34	11	0.002	0
1.618	10	1.622	35	11	0.004	1
1.536	15	1.536	33	11	0.000	4
1.479	36	1.482	55	18	0.003	18
1.447	26	1.448	35	11	0.001	15

*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

**Based on XRD-700 ratemeter calibration charts.

†Run at different power so not feasible to be included.

Table 14.7. X-ray Diffraction Data: d-spacings and relative intensities of 180-day "as-cured"* sealed vial samples.

PSU		WES			d-spacing spread	relative intensity (I) spread
d	I	d	c/s**	I	A	
9.83	46	9.75	93	†	0.08	--
5.64	36	5.61	115	23	0.03	13
4.95	34	4.91	188	37	0.04	3
4.72	31	4.71	60	12	0.01	19
4.26	15	4.25	15	3	0.01	12
3.89	43	3.87	125	25	0.02	18
		3.66	30	6	---	--
3.48	22	3.48	56	11	0.00	11
3.35	35	3.35	117	23	0.00	12
3.25	25	3.24	53	10	0.01	15
3.11	29	3.11	100	20	0.00	9
3.04	51	3.03	123	24	0.01	27
2.881	28	2.882	103	20	0.001	8
2.781	91	2.776	214	42	0.005	49
2.747	64	2.743	157	31	0.004	33
2.633	100	2.627	503	100	0.006	0
2.606	39	2.606	126	25	0.000	14
2.568	28	2.562	119	24	0.006	4
2.286	1	2.279	25	5	0.007	4
2.210	32	2.208	91	18	0.002	14
2.156	11	2.151	56	11	0.005	0
2.107	12	2.103	35	7	0.004	5
2.058	4	2.053	30	6	0.005	2
1.930	39	1.928	144	29	0.002	10
1.822	20	1.821	53	10	0.001	10
1.797	24	1.795	81	16	0.002	8
1.765	16	1.762	25	5	0.003	11
1.685	9	1.686	52	10	0.001	1
1.663	7	1.664	40	8	0.001	1
1.575	10	1.574	27	5	0.001	5
1.486	11	1.485	58	12	0.001	1
1.451	3	1.450	30	6	0.001	3

*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

**Based on XRD-700 ratemeter calibration charts.

†Run at different power so not feasible to be included.

Table 14.8. X-ray Diffraction Data: d-spacings and relative intensities of 365-day "as-cured"* sealed vial samples.

PSU		WES			d-spacing spread	relative intensity (I) spread
d	I	d	c/s**	I	A	
9.74	34	9.77	550	†	0.03	—
8.27	22				—	—
7.29	8				—	—
5.61	30	5.61	166	65	0.00	35
4.92	15	4.91	219	83	0.01	68
4.69	19	4.71	103	39	0.02	20
4.27	26	4.26	23	9	0.01	17
3.87	43	3.89	146	55	0.02	12
		3.67	28	11	—	—
3.60	26	3.61	45	17	0.01	9
3.46	11	3.48	71	27	0.02	16
3.34	41	3.34	95	36	0.00	5
3.24	16	3.24	68	26	0.00	10
3.06	63	3.11	111	42	0.05	21
3.02	47	3.08	119	45	0.01	2
2.96	58	2.976	79	30	0.01	28
2.87	38	2.877	89	34	0.00	4
2.77	98	2.774	202	76	0.00	22
2.73	78	2.744	114	43	0.01	35
2.68	61	2.688	83	31	0.03	40
2.63	100	2.632	264	100	0.00	0
2.60	47	2.614	126	48	0.01	1
2.56	46	2.564	128	48	0.00	2
2.44	2	2.453	31	12	0.01	10
		2.434	26	10	—	—
2.40	25	2.407	28	11	0.00	14
2.36	20	2.316	26	10	0.05	10
2.31	17				—	—
2.27	13	2.284	27	10	0.01	3
2.20	57	2.207	93	35	0.00	22
2.18	45	2.183	44	17	0.00	28
2.15	24	2.153	69	26	0.00	2
2.12	36				—	—
2.10	13	2.107	36	14	0.00	1
2.05	37	2.058	38	14	0.00	23
1.97	18	1.979	20	8	0.00	10
1.94	42	1.942	35	13	0.00	29
1.92	66	1.925	135	51	0.00	15
1.82	68	1.823	50	19	0.00	49
1.81	46	1.814	45	17	0.00	29
1.79	42	1.795	105	40	0.00	2
1.76	28	1.762	35	13	0.00	15
1.68	34	1.686	53	20	0.00	14
1.66	22	1.664	45	17	0.00	5
1.62	28	1.623	29	11	0.00	17
1.57	11	1.574	26	10	0.00	1
1.53	17	1.539	29	11	0.00	6
1.48	42	1.484	42	16	0.00	26
1.44	25	1.447	14	5	0.00	20
		1.314	13	10	—	—

*The samples were cut and x-rayed as soon as possible after removal from the curing chamber.

**Based on XRD-700 ratemeter calibration charts.

†Run at different power so not feasible to be included.

Since this report deals with an interlaboratory comparison of results, tabular listings of data are insufficient in that they are only indicators of the accuracy and precision of measurement between two laboratories. The data deal with machine and operator, relying heavily on standard techniques (SOP) and calibration procedures. What is of more interest is the comparison of judgment in assigning various phase identities to each of the listed peaks and relative amounts present to each identified phase. It would be a very tedious exercise to prepare comparisons for all of the data, therefore only one set of PSU and WES data have been compared. The 56-day data previously given in Table 14.5 are reworked and each peak has had an associated phase identity listed with it (Table 14.9). When overlapping peaks were thought to be present, multiple labels have been given to each peak. Phase data for all samples, namely those hydrated for 3, 7, 28, 56, 90, 180 (181), and 365 days, have also been summarized by each laboratory and are listed in order of decreasing intensity for each time period (Table 14.10). These data deal with sealed vial-cured samples x-rayed in the "as-cured" condition. Although identities of phases present may, in some cases, appear to be assigned on a rather tenuous basis such as the presence of a single d-spacing or 2θ value, the data in Tables 14.9 and 14.10 as well as the following discussions are in fact based upon the evaluation of the full patterns as typified by the examples given in Figures 14.1 and 14.2. A specific example is the identification of the chloroaluminate phase by the 7.8 Å peak which is unique to this phase in these patterns. It is indicated by an arrow in Figure 14.1(e) and 14.2(a).

14.2.1 WES - The x-ray diffraction (XRD) patterns show the 3- and 7-day-old grout samples to be similar. Gypsum was present in the 3-day-old sample, but was not present in the 7-day-old sample. There was more tetracalcium-aluminate dichloride-10-hydrate (chloroaluminate)* and ettringite in the 7-day-old sample than in the 3-day-old sample. Examination of XRD patterns at later ages (see Fig. 14.1) showed they remained generally similar. The following was observed:

a: Peaks due to unhydrated cement persisted, but did become weaker as hydration continued.

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*Note that chloroaluminate and Friedel's salt are used interchangeably since they are in fact different names of the same material. See Section 21.0, Glossary of Phases, for additional data on nomenclature of phases and chemistry when reading this and following sections.

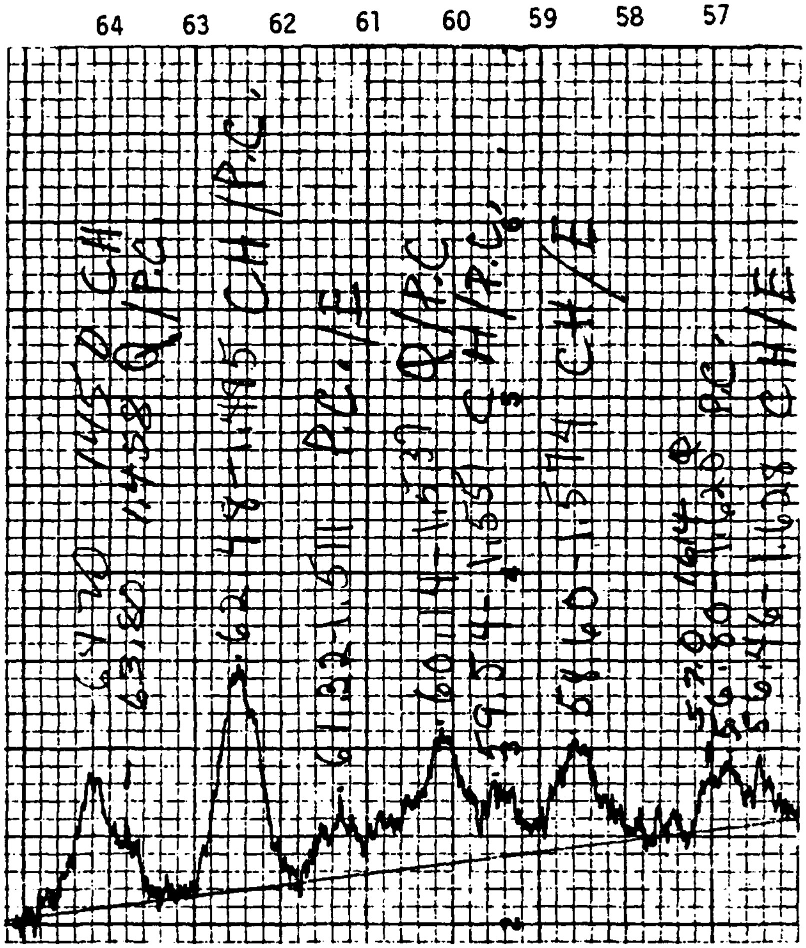
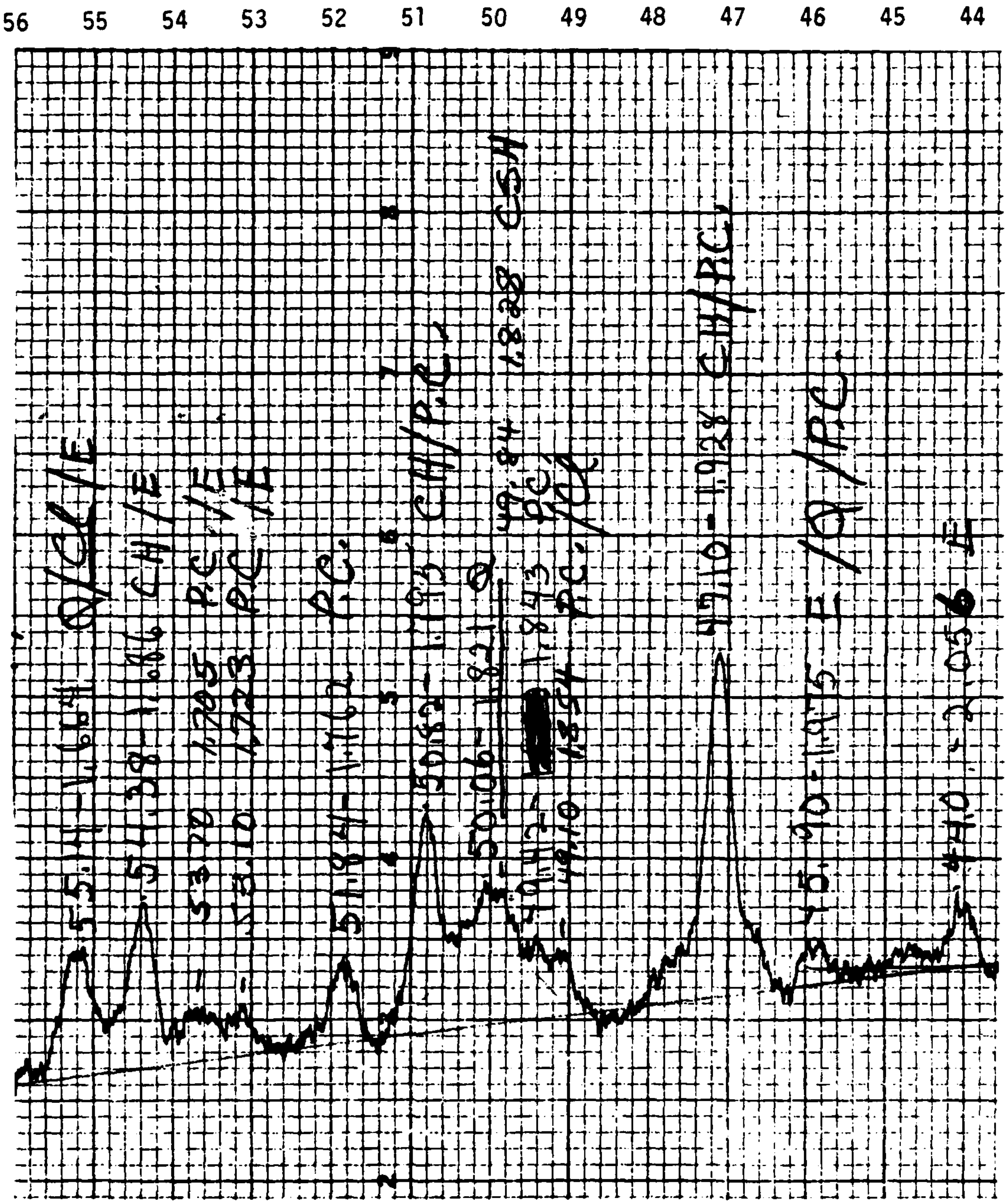
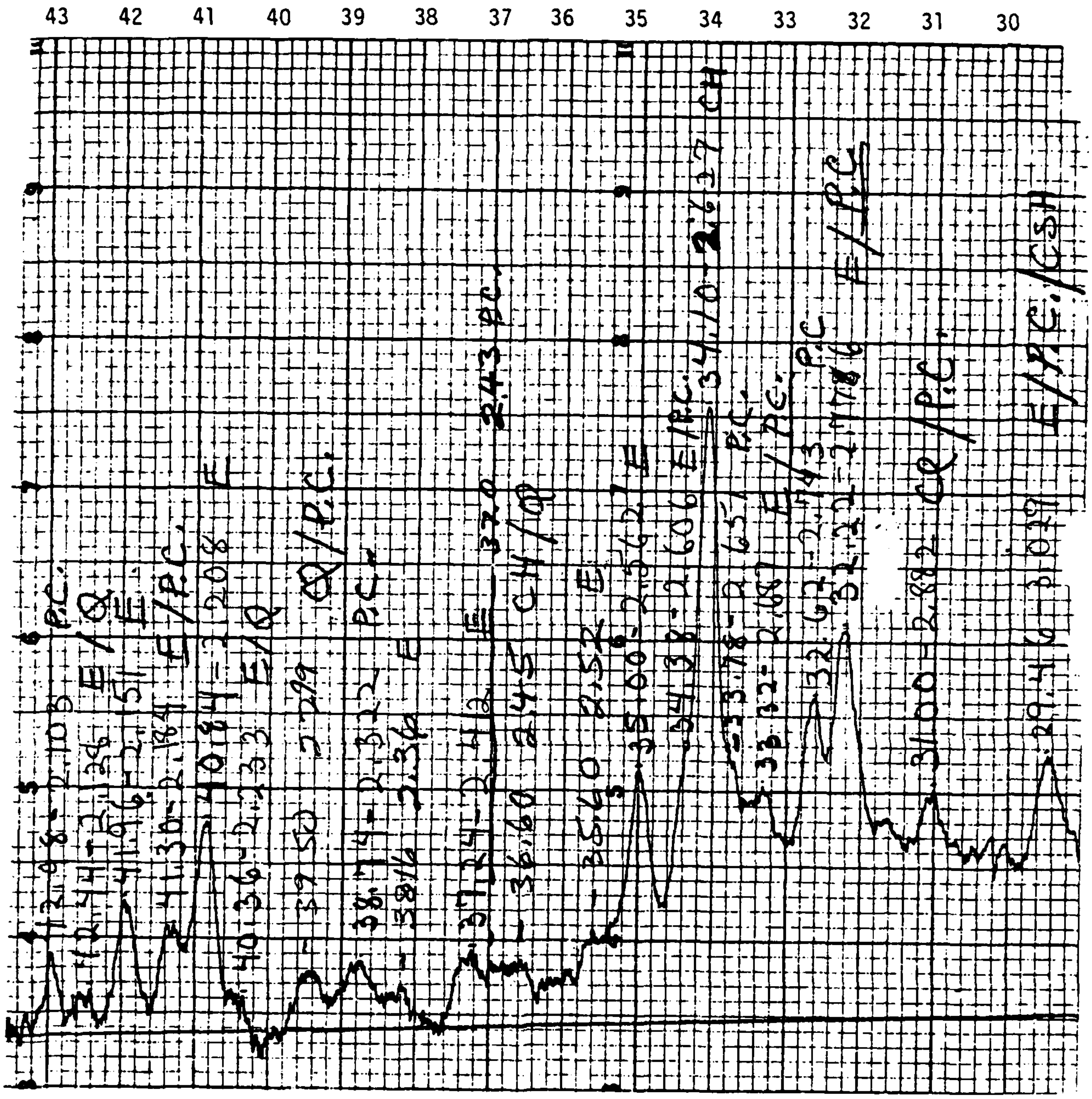


Figure 14.1(a). X-ray diffraction chart (WES), sample and test conditions stated on Figure 14.1(e). Work sheet for identification of phases; see text


56
55
54
53
52
51
50
49
48
47
46
45
44
2
3
4
5
6
7
8
9
55.14-1.664 Q/CH/E
54.38-1.686 CH/E
53.78 1.705 PC/E
53.10 1.723 PC/E
51.84-1.762 PC
50.62-1.793 CH/P.C.
50.06-1.821 Q
49.42-1.843 PC
49.10 1.854 PC/Q
49.84 1.828 CSH
47.10-1.928 CH/PC
45.90-1.975 E/Q/PC
44.10-2.056 E

(b)



(c)

COMPOSITION

E = ETTRINGITE

CH = CALCIUM HYDROXIDE

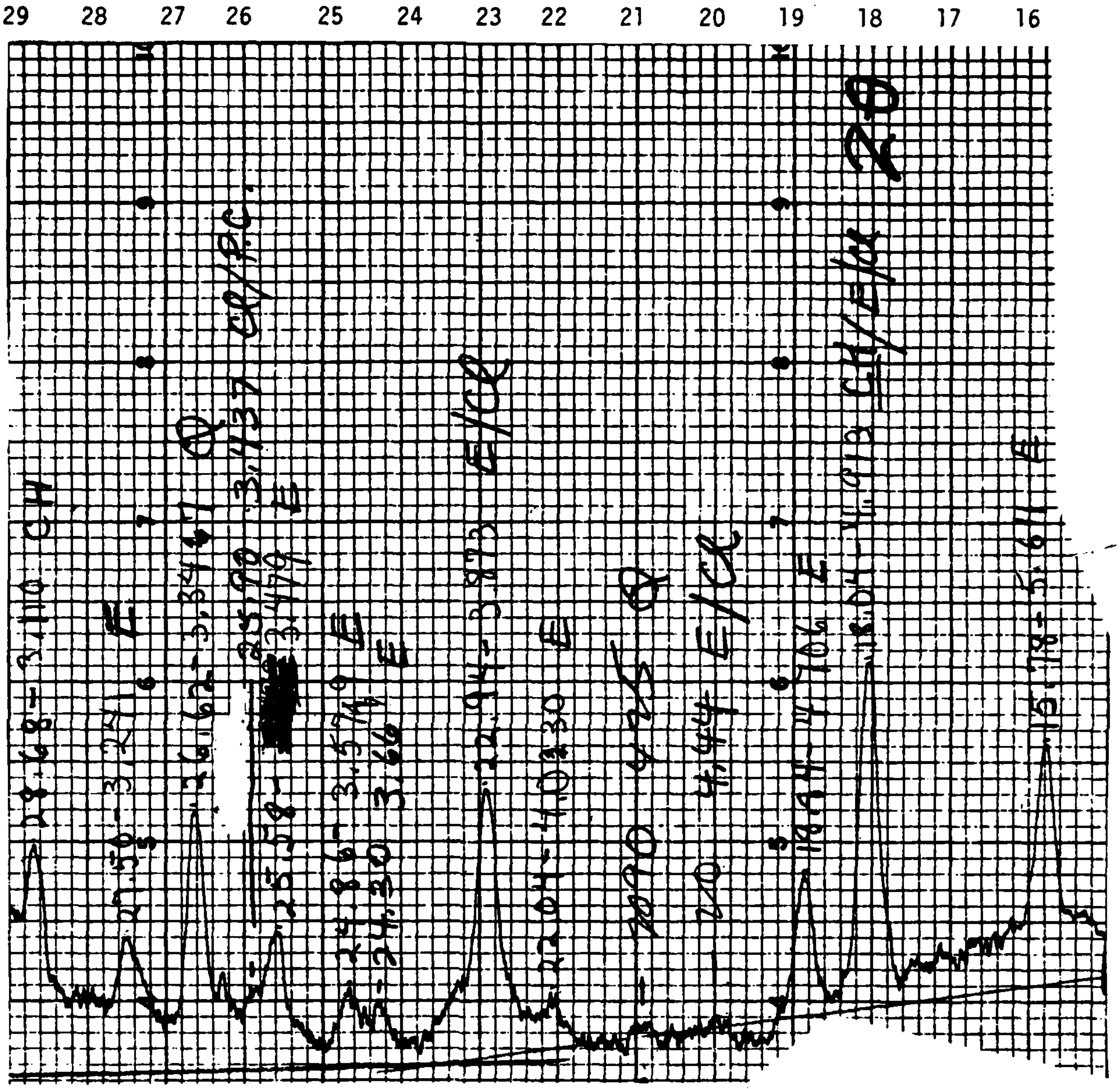
Cℓ = TETRACALCIUM ALUMINATE DICHLORIDE-10-HYDRATE ("Chloroaluminate," "Friedel's Salt")

CSH = CALCIUM SILICATE HYDRATE

H = TETRACALCIUM ALUMINATE HEMICARBONATE-12-HYDRATE

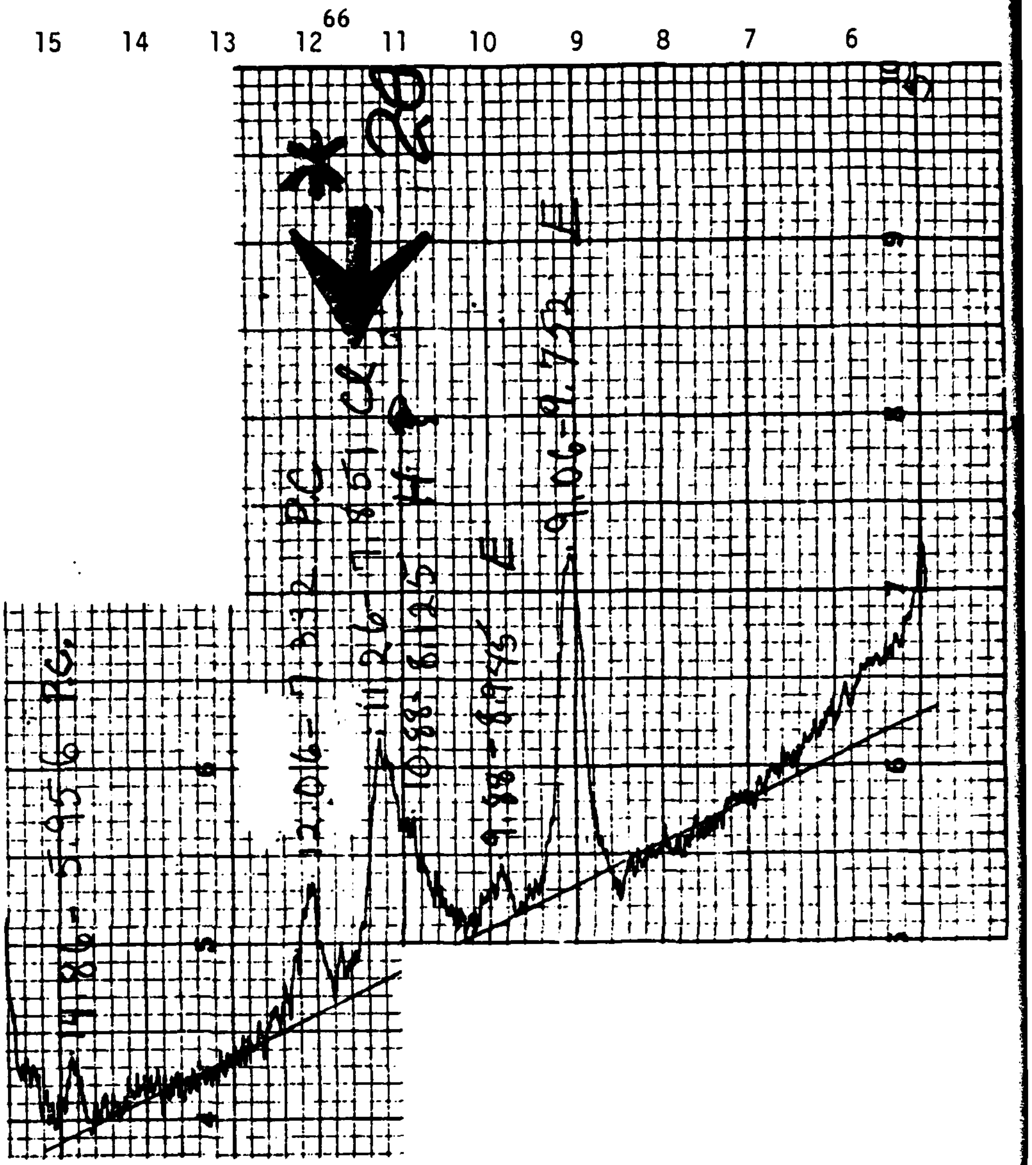
PC = UNHYDRATED PORTLAND CEMENT

Q = QUARTZ (ex FLY ASH)



Arrow Indicates a Change to High Power ~50 KVCP ~21ma; Scale Exp.-331 20° zero offset; 3° Beam Slit Standardized Here

(d)



181 day age

XRD-7 Sample Data: sawed slab of vials (M96D) in* Vapor Hood w/static N_2 and $Ba(OH)_2$ soaked sponge

Sample Length: 2 in. Standardized yes

Project PSU-WES CO-OP Memo No. 2096-D

Counter tube 10A Atmosphere * Rel. Hum

Slits: Beam 1° Soller 3° Detector 0.2 Filter Ni

KVCP 35 MA 21 Target Cu T.Angle 4° Port side

Range log 4K Time Constant 8sec. Scale Expan. 372

PHS Inat 91% E 0.2 DE 0.6 CT 2540 Gain 4

Speed 2°/min Date 23 March '81 Done by JR

no zero offset

Key: 1st No.=degrees 2Θ
2nd No.=d-spacings in Å

(e)

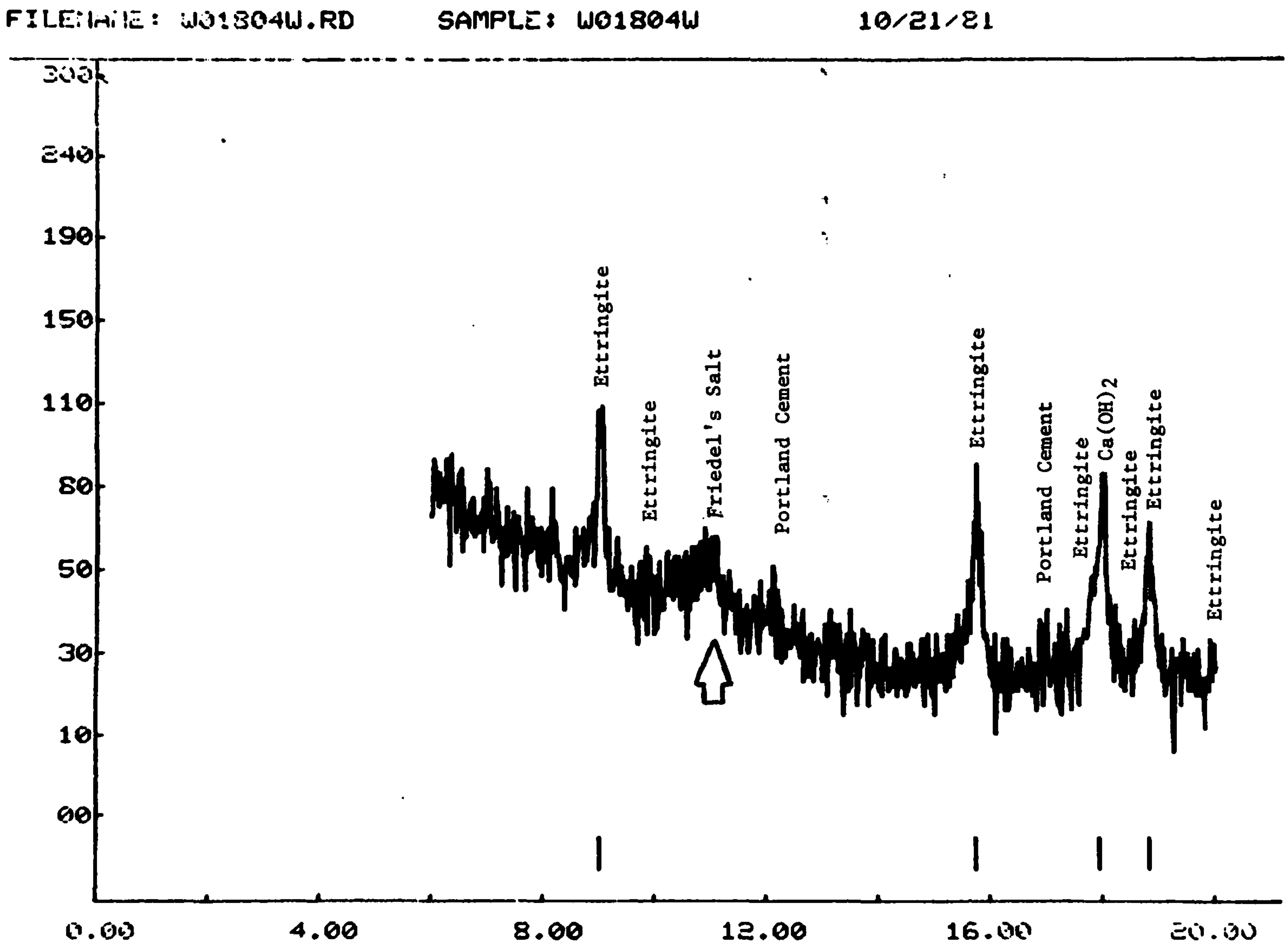
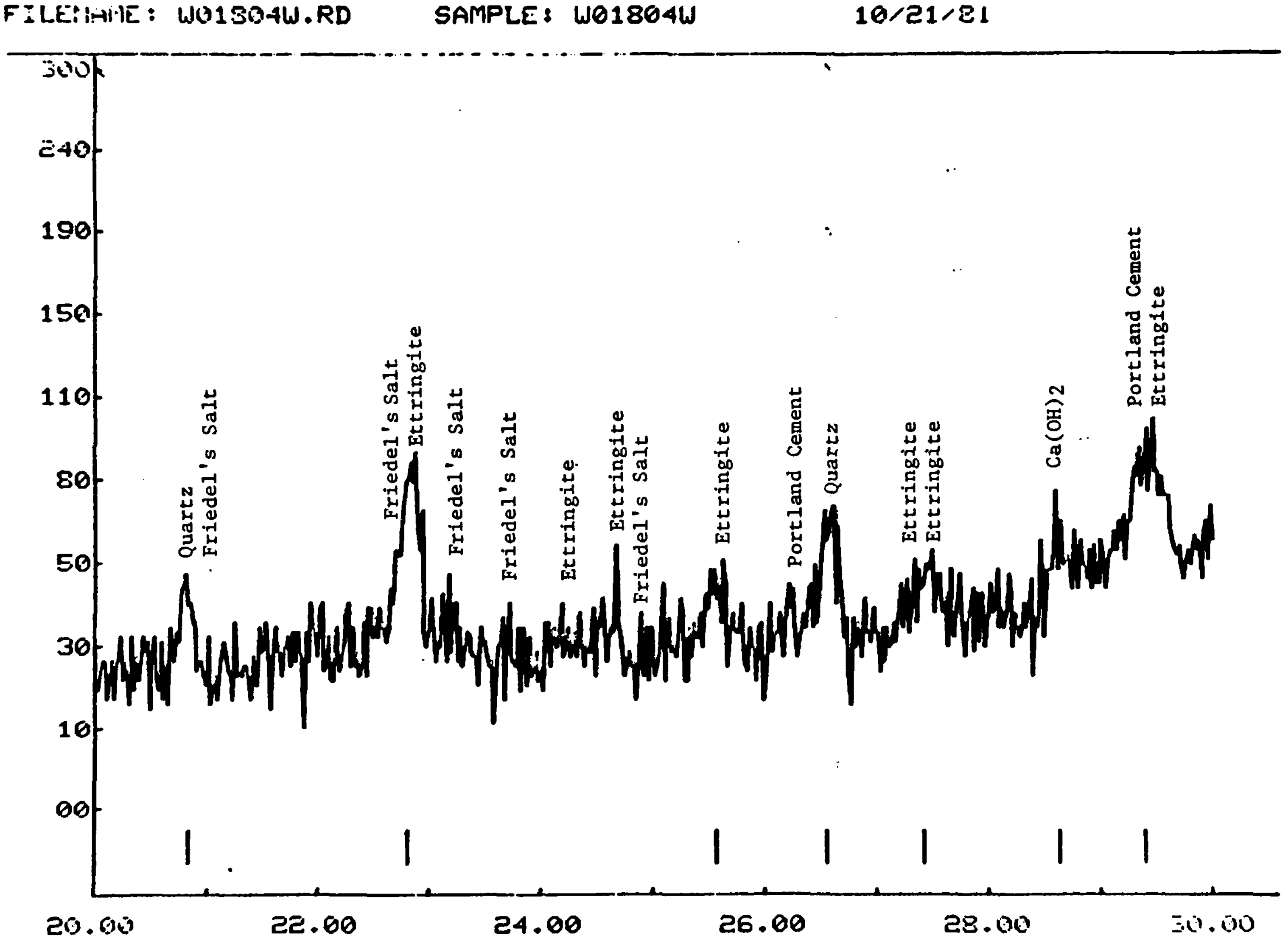


Figure 14.2(a) 180-day "as-cured" sealed vial x-ray diffraction pattern.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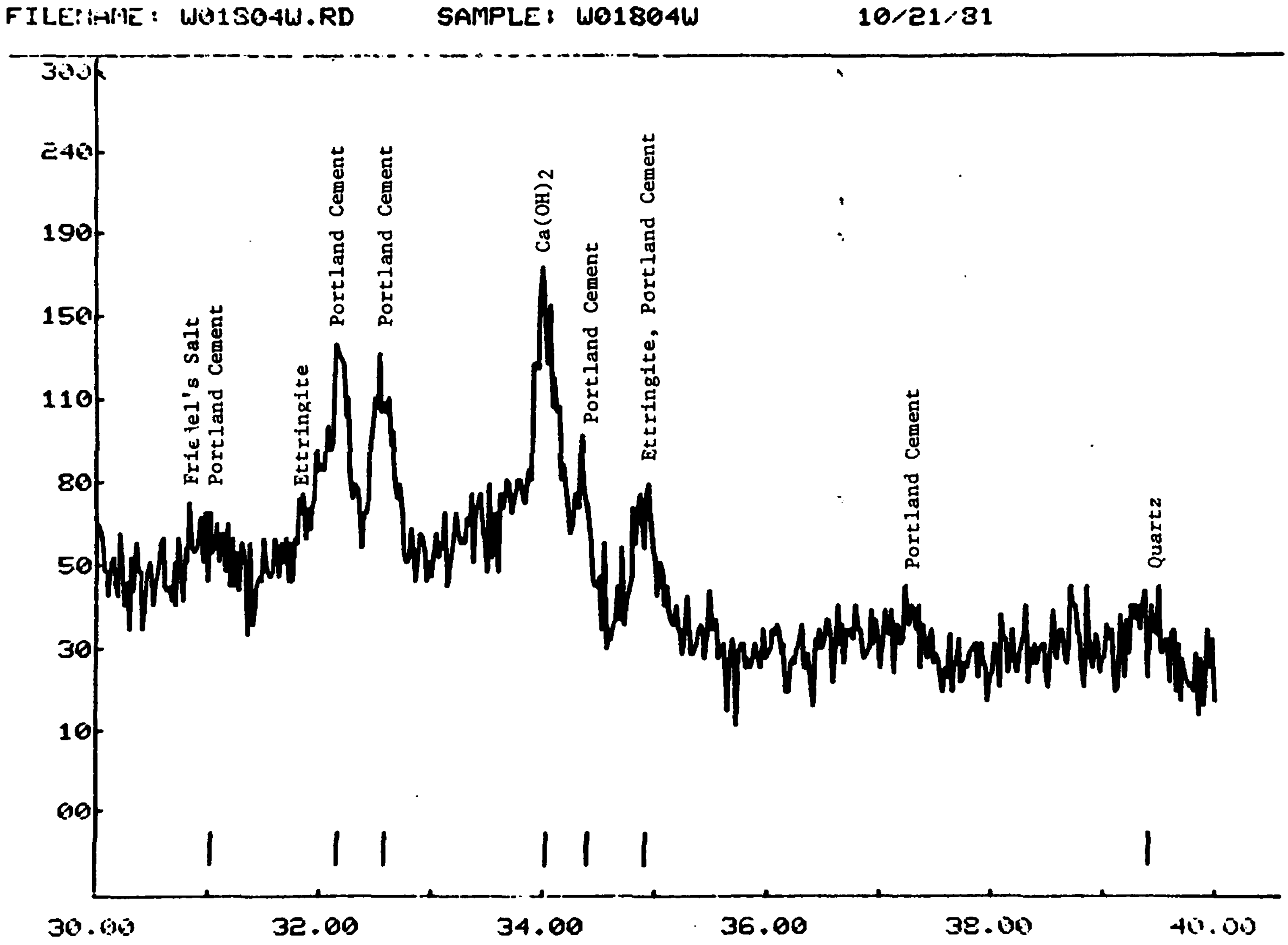
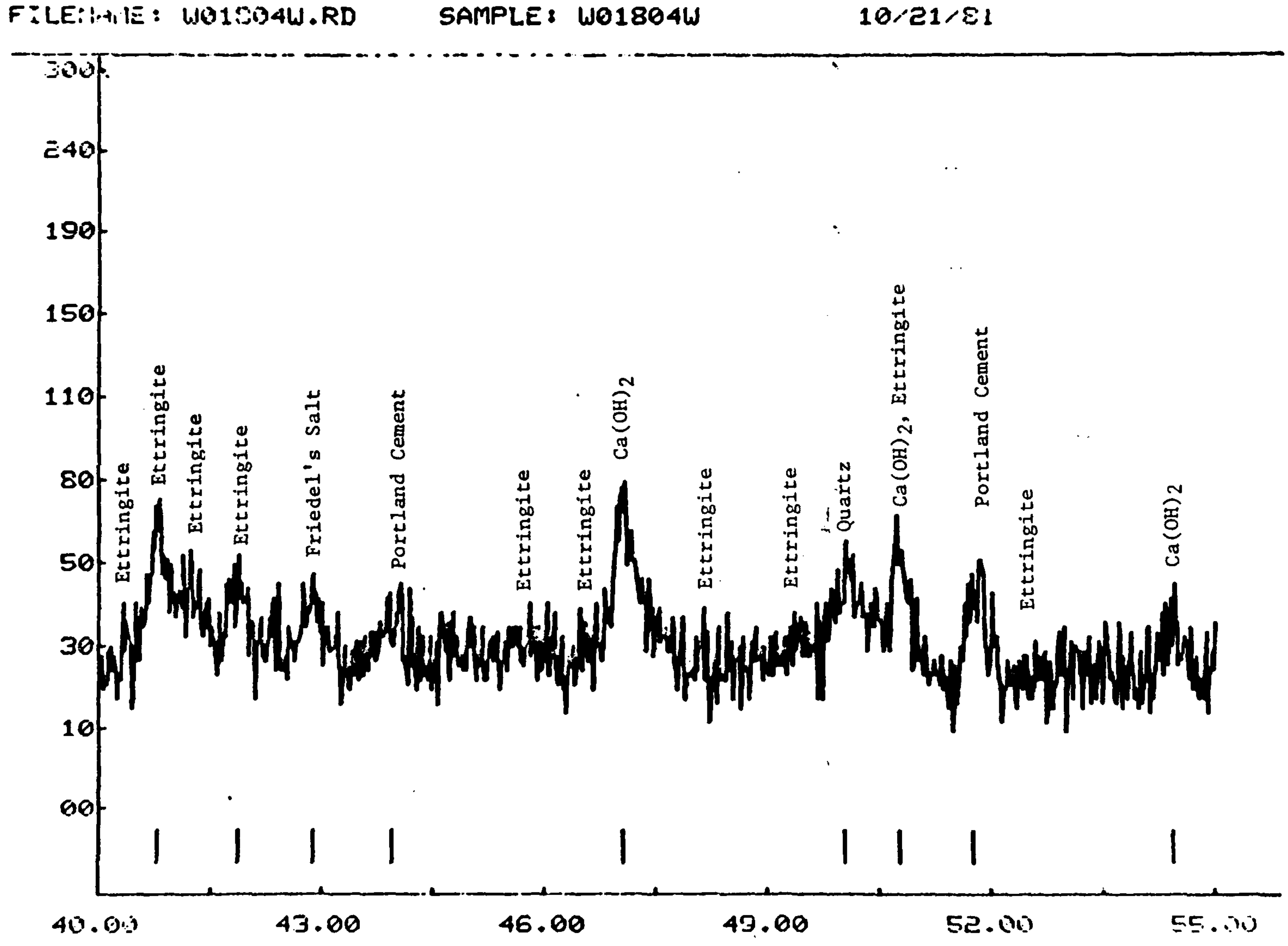
SAMPLE: W01804W
10/21/81
300
240
190
150
110
80
50
30
10
00
20.00
22.00
24.00
26.00
28.00
30.00
Quartz
Friedel's Salt
Friedel's Salt
Ettringite
Friedel's Salt
Friedel's Salt
Ettringite
Ettringite
Friedel's Salt
Ettringite
Portland Cement
Quartz
Ettringite
Ettringite
Ca(OH)2
Portland Cement
Ettringite

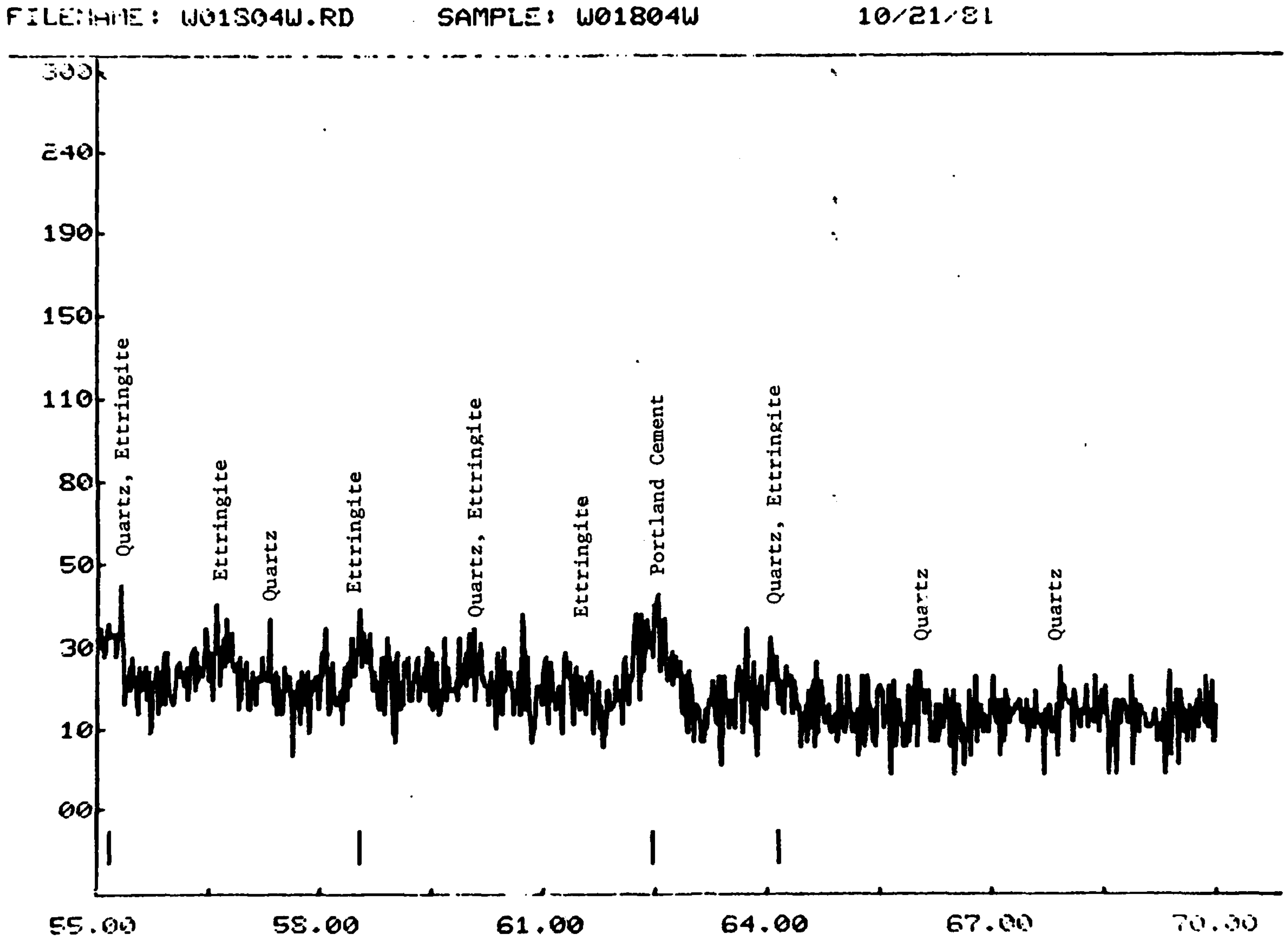
14.2(b)


FILENAME: W01S04W.RD
SAMPLE: W01804W
10/21/81
300
240
190
150
110
80
50
30
10
00
Friedel's Salt
Portland Cement
Ettringite
Portland Cement
Portland Cement
Ca(OH)2
Portland Cement
Ettringite, Portland Cement
Portland Cement
Quartz
30.00
32.00
34.00
36.00
38.00
40.00

14.2(c)


FILENAME: W01S04W.RD
SAMPLE: W01804W
10/21/81
300
240
190
150
110
80
50
30
10
00
Ettringite
Ettringite
Ettringite
Ettringite
Friedel's Salt
Portland Cement
Ettringite
Ettringite
Ca(OH)2
Ettringite
Ettringite
Quartz
Ca(OH)2, Ettringite
Portland Cement
Ettringite
Ca(OH)2
40.00
43.00
46.00
49.00
52.00
55.00

14.2(d)


FILENAME: W01S04W.RD
SAMPLE: W01804W
10/21/81
300
240
190
150
110
80
50
30
10
00
Quartz, Ettringite
Ettringite
Quartz
Ettringite
Quartz, Ettringite
Ettringite
Portland Cement
Quartz, Ettringite
Quartz
Quartz
55.00
58.00
61.00
64.00
67.00
70.30

14.2(e)

b: One or more weak, broad peaks due to semi-amorphous calcium silicate hydrate (C-S-H) appeared with increasing age.

c: Ettringite peaks persisted relatively unchanged with time. There seemed to be significantly less ettringite at 28 and 90 days by the intensity of the 9.7A peak, but this may have been a sampling effect. There was doubtless some conversion of ettringite to chloroaluminate since the 7.8A peak of chloroaluminate was weakest at 3 days age and increased to a fairly constant level thereafter and was always present in the x-ray patterns.

d: Calcium hydroxide (CH) was always present in large amounts.

e: Quartz from the fly ash was always present.

f: Salt (NaCl) was tentatively identified in most patterns.

g: No forms of calcium sulfate phases were detected after the 3-day age.

h: A small amount of tetracalcium aluminate monosulfate-12-hydrate (monosulfoaluminate) was possibly often present based on the presence of a weak peak at about 8.9A.

i: The common presence of a weak unresolved peak at about 8.2A on the low-angle shoulder of the 7.8A chloroaluminate peak suggested the presence of a small amount of tetracalcium aluminate hemicarbonate-12-hydrate.

j: In general, phase composition of the grout samples was considered normal for the mixture.

After the cube was broken at the one-year age and had been stored in fresh water for 48 hr the inner surface of a fragment was smoothed and examined by XRD. Comparison of this pattern with that of the vial of one-year-old grout showed that the cube that had been stored in lime water rather than sealed as the vial had been contained more ettringite, less chloroaluminate, and was more hydrated. These changes were what would be expected for the differences in storage conditions. None of the plastic vials showed evident distortion or cracking of the contents while most of the samples (cubes, bars) exposed to lime water during storage had cracked. This is taken to mean that the low water content grout in sealed vials experienced less expansion.

14.2.2 PSU - Disk samples cut from the mid-portion of the cement paste cylinders hydrated in sealed glass vials were studied. They were cut perpendicular to the long axis of the cylinder and were, in intent, similar to the rectangular slabs used by WES in their study. The x-ray patterns were run in increments of 0.02°2θ for 0.6 sec, in the "as-cured" condition. As estimated from peak intensities, other than residual cement phases (alite and belite), ettringite was the most abundant crystalline hydration product in the 3-, 7- and

Table 14.9. A Peak-by-Peak Interlaboratory Comparison of Peak Intensities of 56-day X-ray Diffraction Data.

PSU			WES			
d	I	phases	d	c/s	I	phases
9.61	24	ETT	9.75	141	*	ETT
6.23	7	---	7.31	19	*	AF
5.57	21	ETT	5.60	122	35	ETT
4.89	29	CH,ETT	4.91	205	59	CH,FS,EH
4.67	15	ETT	4.69	66	19	ETT
3.86	36	ETT,FS	3.87	120	35	ETT,FS
			3.65	24	7	AF
3.59	9	ETT	3.60	33	10	ETT
3.48	32	ETT	3.47	59	17	ETT
3.33	46	Q	3.34	173	50	Q
3.22	15	ETT	3.23	58	17	ETT
3.10	27	CH	3.11	94	27	CH
3.02	43	ETT,A,C-S-H	3.02	109	32	ETT,A,C-S-H
2.870	29	B,FS	2.875	78	23	B,FS
2.767	79	ETT,B,A	2.769	245	71	ETT,A,B
2.731	76	A,B	2.738	133	38	A,B
2.621	100	CH,ETT	2.624	345	100	CH,ETT,FS
2.598	74	A,B,	2.602	104	30	ETT,A
2.556	37	ETT	2.562	104	30	ETT
2.402	12	ETT	2.404	36	10	ETT
2.313	11	B,A,FS	2.316	32	9	ETT,B,A
2.278	13	Q,B,A	2.283	29	8	Q,FS
2.204	42	ETT	2.204	92	27	ETT,FS,AF
2.176	24	ETT,A,B	2.168	103	30	ETT,A
2.148	25	ETT	2.151	69	20	ETT,FS
2.101	14	B	2.102	42	12	B,ETT,FS
2.053	14	B	2.053	42	12	ETT,FS,AF
1.924	65	CH,A	1.925	117	34	CH,A,FS,AF
1.793	61	CH,A	1.794	77	22	CH,A,EH
1.762	38	A	1.759	41	12	A,EH
1.684	29	CH,A	1.685	40	12	CH,A,EH
1.660	23	ETT	1.663	34	10	ETT,Q,FS
1.622	29	A,ETT	1.620	25	7	A
1.572	26	ETT	1.574	28	8	ETT
1.488	32	A	1.489	37	11	A
1.481	44		1.483	44	13	CH
1.447	23	CH,ETT	1.448	24	7	CH,ETT
1.313	10	ETT	**	--	--	

*Run at different power so not feasible to be included.
**Pattern not run this far.

CH = $Ca(OH)_2$
A = Alite
B = Belite
ETT = Ettringite
HF = Calcium aluminoferrite (from cement)

C-S-H = Calcium silicate hydrate
FS = Friedel's salt, chloro-aluminate, tetracalcium aluminate-dichloride-10-hydrate
Q = quartz

28-day samples; calcium hydroxide [$Ca(OH)_2$] was the second most abundant hydration phase. From 56 to 90 days, the intensity of ettringite peaks decreased relative to calcium hydroxide (a trend similar to the one observed by WES), and only at 180 and 365 days did the ettringite once again regain prominence as a major hydration phase, and at the same time also became the major phase in the cement paste. Friedel's salt began to appear at 28 days and gradually increased in intensity through 365 days. In the sealed vial hydration, the limited amount of water present combined with the salt in the original mixture, began to favor the formation of the lower water-containing hydration product, Friedel's salt, over the very water-rich ettringite. In addition to the major phases, occasionally minor amounts of calcite (due to slight carbonation), quartz (from the fly ash), tetracalcium aluminate monosulfate hydrate ($C_4A\bar{S}H_{12}$), and poorly crystalline calcium silicate hydrate (C-S-H) were also detected.

14.2.3 Interlaboratory Comparison

Table 14.10 shows a comparison of crystalline phases detected at the two laboratories in the grout at different ages. While most of the major phases were identified, their sequence is not always the same since the listing in Table 14.10 is based on peak intensities and these may be affected by factors other than the amount present. Due to the complexity of the cement grout system, minor phases were often difficult to resolve by x-ray diffraction analysis.

14.2.4 Additional PSU X-ray Diffraction Data

14.2.4.1. Introduction - In addition to these data, PSU also collected data for three other conditions of hydration and drying. These data were collected in order to illustrate possible differences in results as a function of borehole hydration conditions or state of drying. To investigate the effect of environment, two samples were prepared for each curing time as follows: 1) A 1-in (25.4-mm) OD x 2-in. (50.8-mm) long cylinder was allowed to hydrate at temperature (38°C) in a saturated solution of $Ca(OH)_2$ which approximated hydration in a "wet" low-CO_2 borehole environment, and 2) a sample was cured in a sealed glass vial (shell vial) which represented a condition nearer a "dry" borehole environment. In addition, in order to understand the effects of drying, two disks were cut from each of the above cylinders. Since they were

Table 14.10. An Interlaboratory Comparison of Hydration Data for Sealed-vial Cured Samples. Phases listed in order of decreasing peak intensity.

Length of Hydration	PSU	WES
3 days	Unhydrated P.C. Ettringite $Ca(OH)_2$ Quartz C-S-H Monosulfoaluminate (?) Calcite (?)	Ettringite CH Unhydrated P.C. (including MgO) Quartz Gypsum Chloroaluminate (FS) Monosulfoaluminate (?) Calcite(?)
7 days	Unhydrated P.C. Ettringite CH Quartz C-S-H Monosulfoaluminate (?) Calcite (?)	Ettringite Unhydrated P.C. (including MgO) CH Quartz Monosulfoaluminate (?) Chloroaluminate (FS) Calcite (?)
28 days	Unhydrated P.C. Ettringite CH Calcite Quartz Friedel's salt (CA) C-S-H Monosulfoaluminate (?)	CH Chloroaluminate (FS) Ettringite Unhydrated P.C. (possibly including MgO) Quartz C-S-H Calcite (?) Salt (?)
56 days	Unhydrated P.C. $Ca(OH)_2$ Ettringite Quartz C-S-H Friedel's salt (Tr) Monosulfoaluminate (?)	CH Ettringite Chloroaluminate (FS) Unhydrated P.C. Quartz C-S-H Monosulfoaluminate (?) Salt (?)

Table 14.10 (continued)

Length of Hydration	PSU	WES
90 days	Unhydrated P.C. $Ca(OH)_2$ Ettringite Quartz C-S-H Friedel's salt (CA) Monosulfoaluminate	CH Chloroaluminate (FS) Ettringite Unhydrated P.C. Quartz C-S-H Salt (?)
180,181 days	Ettringite CH Unhydrated P.C. Quartz Friedel's salt (CA) C-S-H Monosulfoaluminate (?) Calcite (?)	Chloroaluminate (FS) Ettringite CH Unhydrated P.C. Monosulfoaluminate C-S-H Quartz Calcite (?) Salt (?)
365 days	Ettringite Unhydrated P.C. CH Quartz Friedel's salt (CA)* C-S-H Gypsum (?)	Ettringite CH Chloroaluminate (FS) Unhydrated P.C. C-S-H Quartz Hemicarbonate (?)

CH = calcium hydroxide
Unhydrated P.C. = unhydrated portland cement
CA - FS = tetracalcium aluminate dichloride-10-hydrate
Tr = trace
? = uncertain if present
*Unknown peak at 10.71°. Might be an intermediate between ettringite and Friedel's salt having slightly greater water content than Friedel's salt.

neighboring cuts, the x-ray data collected from each was nearly identical. Assuming this to be true, one sample was run in the "as-cured" condition and its neighbor was dried before x-raying. Thus each hydration time had associated with it four sets of data. These data are presented in Table 14.11. Phases identified in each of these samples are listed in order of decreasing peak intensities/abundances. Since unhydrated cement phases (β-C_2S and C_3S) were difficult to separate due to overlapping of peaks, their relative abundances were listed as if they were a single phase (indicated by parentheses).

14.2.4.2 Results of Environment - Comparing the x-ray data given in Table 14.11, columns 1 and 3, it is possible to comment upon the potential effect of a wet versus dry borehole environment, at least in very general terms. In the dry environment, approximated by the column 1 data, ettringite and $Ca(OH)_2$ were the major hydration phases very early in the hydration history of the mixture. Their intensities were second only to the residual cement phases. At 56 and 90 days ettringite was less intense than $Ca(OH)_2$, regaining prominence by 180 days. The limited water present in the sealed vial samples led to the formation of small amounts of Friedel's salt after 28 days of hydration, presumably at the expense of the more water-rich ettringite. In the wet environment (column 3), ettringite was more prominent, over overshadowing $Ca(OH)_2$ and remnant cement phases (7 and 28 days). Once again ettringite intensity decreased at 56 and 90 days regaining prominance at 180 and 365 days. Ettringite was more abundant in the solution cured samples, presumably due to the influx of additional water which favored the production of the water-rich ettringite. Friedel's salt was not observed in these very water- and lime-rich samples. It is concluded that the environment will, indeed, play an important role in the repository sealing operation, influencing final physical and mechanical properties of the emplaced materials.

14.2.4.3 Results of Drying - At first, samples were dried at 60°C in vacuum for up to 15-1/2 hr. However, it soon became evident that drying under these conditions destroyed the ettringite present [see for example, Table 14.11, 3, 7, and 28 day results, for $Ca(OH)_2$ "as-cured" versus 60°C vacuum dry]. As a result, the remaining samples of $Ca(OH)_2$ cured and nearly all shell-vial cured samples were freeze-dried under vacuum at less than 32°C for up to 24 hr.

Comparing columns 1 and 2, it is evident that the freeze drying procedure did not significantly alter the number of phases present or their relative

Table 14.11. X-ray Diffraction Phase Data for Various Hydration Environments and/or States of Drying; phases listed in order of decreasing intensities.

	shell vial "as-cured"	shell vial freeze dried	$Ca(OH)_2$ "as-cured"	$Ca(OH)_2$ 60°C vac.dry*
3 days	$\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Ettringite $Ca(OH)_2$ Quartz C-S-H Ca-mono. (?) Calcite (?)	$\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Ettringite $Ca(OH)_2$ Quartz C-S-H Ca-Mono. (?)	$Ca(OH)_2$ $\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Ettringite Quartz C-S-H Ca-mono. (?) C_4AF (?)	$Ca(OH)_2$ $\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Quartz C-S-H
7 days	$\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Ettringite $Ca(OH)_2$ Quartz C-S-H Ca-Mono. (?) Calcite (?)	$\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Ettringite $Ca(OH)_2$ Quartz C-S-H Ca-mono. (?) Calcite (?)	Ettringite $\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ $Ca(OH)_2$ Quartz C-S-H Ca-mono. (?)	$Ca(OH)_2$ $\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Quartz C-S-H C_4AF (?)
28 days	$\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Ettringite $Ca(OH)_2$ Calcite Quartz Friedel's salt C-S-H Ca-Mono. (?)	$\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ $Ca(OH)_2$ Quartz Ca-Mono. (?) This sample was apparently dried at 60°C in a vacuum which destroyed the ettringite	Ettringite $\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Quartz Ca-mono. (?) C-S-H	$Ca(OH)_2$ $\begin{Bmatrix} C_3S \\ \beta\text{-}C_2S \end{Bmatrix}$ Quartz Calcite C-S-H (tr)

Table 14.11 (continued)

	shell vial "as-cured"	shell vial freeze dry	$Ca(OH)_2$ "as-cured"	$Ca(OH)_2$ freeze dry*
56 days	$\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ $Ca(OH)_2$ Ettringite Quartz C-S-H Friedel's salt Ca-Mono. (?)	$\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ Ettringite $Ca(OH)_2$ Calcite Quartz Friedel's salt C-S-H (tr)	$\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ Ettringite $Ca(OH)_2$ C-S-H Calcite Ca-Mono. (?)	$\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ $Ca(OH)_2$ Ettringite Quartz C-S-H Ca-Mono. (?) Calcite (?)
90 days	$\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ $Ca(OH)_2$ Ettringite Quartz Friedel's salt C-S-H Ca-Mono. (?)	$\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ $Ca(OH)_2$ Ettringite Quartz Friedel's salt C-S-H (tr) Ca-Mono. (?)	$\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ $Ca(OH)_2$ Ettringite Quartz Calcite (?) Calcite (?)	$\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ Ettringite $Ca(OH)_2$ Quartz C-S-H Ca-Monc. (?)
180 days	Ettringite $Ca(OH)_2$ $\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ Quartz Friedel's salt C-S-H Ca-Mono. (?) Calcite (?)	Ettringite $\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ $Ca(OH)_2$ Quartz Friedel's salt	Ettringite $\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ $Ca(OH)_2$ Quartz C-S-H	Ettringite $\begin{Bmatrix}C_3S\\ \beta\text{-}C_2S\end{Bmatrix}$ $Ca(OH)_2$ Quartz C-S-H

Table 14.11 (continued)

	shell vial "as-cured"	shell vial freeze dry	$Ca(OH)_2$ "as-cured"	$Ca(OH)_2$ freeze-dry*
365 days	Ettringite	Ettringite	Ettringite	Ettringite
	$\begin{pmatrix} C_3S \\ \beta\text{-}C_2S \end{pmatrix}$	$\begin{pmatrix} C_3S \\ \beta\text{-}C_2S \end{pmatrix}$	$\begin{pmatrix} C_3S \\ \beta\text{-}C_2S \end{pmatrix}$	$\begin{pmatrix} C_3S \\ \beta\text{-}C_2S \end{pmatrix}$
	$Ca(OH)_2$	$Ca(OH)_2$	$Ca(OH)_2$	$Ca(OH)_2$
	Quartz	Quartz	Quartz	Quartz
	Friedel's salt	Friedel's salt	C-S-H	C-S-H
	C-S-H	C-S-H		Friedel's salt (?)
	gypsum (?)			

---

*Note that 56-day and older samples were freeze dried rather than dried at 60°C in vacuum.

positions in the table. Note that the 28-day freeze dried sample was inadvertently dried at 60°C in vacuum, which destroyed the ettringite.

Comparing data from freeze-dried and "as-cured" samples, columns 3 and 4, from 56 days onward, the results for major phases are fairly consistent. The number of phases present or their relative positions in the table was not affected by the freeze-drying procedure during the later stages of hydration.

It is concluded that next to examining a sample in the "as-cured" condition freeze drying is the best procedure for preserving samples for future analyses. Relative to the "as-cured" sample, relative intensities of phases which are very close in abundance may vary in amplitude, but all phases are preserved.

15.0 Physical and Mechanical Properties of Cured Specimens

15.1 Compressive Strength

15.1.1 PSU - Samples were prepared according to Sections 5.1 and 6.1.1. The specimens in the sealed molds were allowed to cure at 38°C, completely immersed in tap water for 24 hr. Upon demolding, they were surface dried in air, and weighed again immersed in freshly boiled deionized water. Samples were then returned to the 38°C chamber and allowed to continue curing in saturated $Ca(OH)_2$ solution for the allotted amount of time.

Compressive strength testing was accomplished according to ASTM C 109 using a 120,000-lb Tinius-Olsen screw-type compression tester, loading at 0.025-in./min.

15.1.2 WES - Compression testing was according to ASTM C 109.

15.1.3 Results

Results for both laboratories to 365 days are given in Table 15.1. PSU puddled the mixture and used the standard paddle for mixing, whereas WES used a wire whip and did not consolidate the sample. The potential for air entrainment with the whip seems to explain the observed higher PSU compressive strengths.

15.1.4 Discussion

Both laboratories reported that the unrestrained cubes began to show evidence of cracking at various stages of curing. This seems reasonable in light of the fact that the mixture studied was intended to be expansive and the cubes were unrestrained. The compressive strength data are summarized in Figure 15.1. At the earlier ages, the PSU cubes were slightly stronger than their WES counterparts in part due to sample compaction techniques used by PSU. The WES samples diminished in strength between 28 and 56 days by less than 2 percent, while the PSU samples tended to resist cracking until beyond the 56-day age. However, at 90 days, the development of cracks caused the compressive strength of the PSU samples to diminish by nearly 50 percent. The very much greater strength drop of the PSU grout may have been related in part to the higher maximum tensile strengths attained for the samples, their abilities to resist expansion, and the magnitudes of strain attained before cracking. It was observed by examining samples

Table 15.1. Compressive Strength of 2-in. (50.8-mm) Cubes of Mixture Cured at 38°C in Saturated $Ca(OH)_2$ Solution, psi (MPa).

3 Day

	PSU (801667)		WES	
	Batch #2		Batch #1	Batch #2
	7425		6208	6248
	7365		6258	6380
	7230		6298	6242
	7425			
	7305			
	7350			
	7170			
$\bar{x}$ =	7324	$\bar{x}$ =	6255	6290
	(50.5)		(43.1)	(43.4)
σ' =	96	σ' =	45	78
	(0.7)		(0.3)	(0.5)
V,%* =	1.32	V,%* =	0.72	1.24
V =	**	$\bar{x}$ =	6272	
			(43.2)	
		V,%† =	0.56	

7 day

	PSU (801664)		WES	
	Batch #1		Batch #1	Batch #2
	9450		8435	8078
	9150		8370	8128
	9420		8360	8182
	9465			
	9705			
	9555			
	9465			
$\bar{x}$ =	9459	$\bar{x}$ =	8388	8129
	(65.2)		(57.8)	(56.0)
σ' =	167	σ' =	41	52
	(1.2)		(0.3)	(0.4)
V,%* =	1.76	V,%* =	0.49	0.64
V =	**	$\bar{x}$ =	8259	
		V,%† =	3.13	

See notes on page 85.

Table 15.1 (continued)

28 Day		56 Day	
PSU (801665)	WES	PSU (801668)	WES
Batch #1		Batch #2	
12390 13485 13050 13710 13110 13740 13575 $\bar{x}$ = 13294 (91.7) σ' = 483 (3.3) V,%* = 3.70 V = **	12130 12310 12020 $\bar{x}$ = 12150 (83.8) σ' = 146 (1.0) V,%* = 1.20	16020 15930 15960 15000 15390 $\bar{x}$ = 15625 (107.7) σ' = 409 (2.8) V,%* = 2.60	12000 12120 11800 $\bar{x}$ = 11970 (82.5) σ' = 161 (1.1) V%* = 1.33

90 Day		180 or 181 Day	
PSU (81666)	WES	PSU (801669)	WES
Batch #1		Batch #2	
9270 8550 $\bar{x}$ = 8910 (61.5) σ' = 509 (3.5) V,%* = 5.71	13320 13690 12720 $\bar{x}$ = 13240 (91.3) σ' = 490 (3.4) V,%* = 3.70	13170 14070 14070 13950 12300 $\bar{x}$ = 13512 (93.2) σ' = 775 (5.31) V,%* = 5.73	14250 14850 14280 $\bar{x}$ = 14460 (99.7) σ' = 338 (2.3) V,%* = 2.34

See notes on page 85.

Table 15.1 (continued)

365 Day	
PSU (801670)	WES
Batch #2	
11700 12510 12000	11,180[††]
$\bar{x}$ = 12070 (83.2)	
σ' = 409 (2.8)	
V%,[*] = 3.39	

---

[*] Single laboratory within batch coefficient variation (1S%), maximum (ASTM C 109) = 3.8%.

[**] V between batches cannot be calculated for PSU data at any age since all specimens tested at any one age came from the same batch and the 7-, 28- and 90-day specimens came from a different batch than the batch from which the 3-, 56-, 180- and 365-day specimens came.

[†] Allowable maximum between batch coefficient of variation (D2S%) (ASTM C 109) = 10.7%.

[††] Only a single cube was broken at 365 days.

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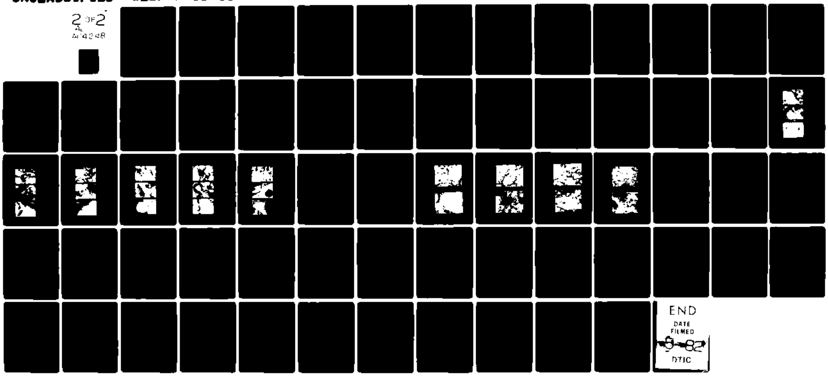

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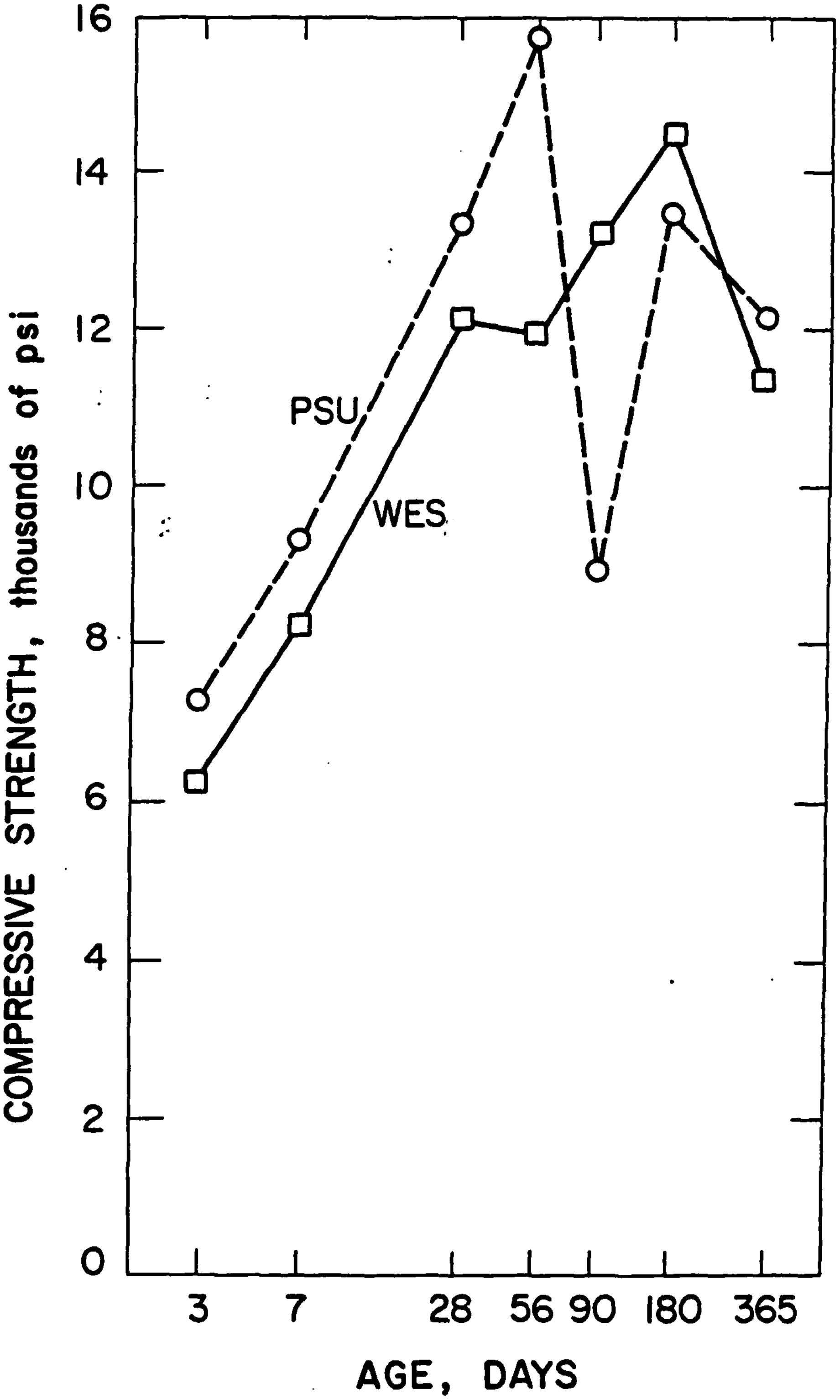

Fig. 15.1 Change in cube strength with age.

after testing that the cracks which had been formed earlier began to show signs of renewed hydration during later curing. Once new surfaces were exposed to the curing solution, additional hydration products formed, tending to fill the cracks that had formed. This may, in part, account for the regain of strength up to 180 days. Since the ultimate use of these materials would be in a restrained situation, the data and observations regarding restrained expansion which are presented later in the report (Section 15.5) have particular importance.

15.1.5 Within-Laboratory Precision

Within-batch single-laboratory coefficients of variation (1S%) as given in ASTM C 109 have been calculated and shown on Table 15.1. Those for PSU at 90 and 180 days (after cubes had cracked) exceed the 3.8% stated as maximum in C 109; they are 5.71 and 5.73. All WES data have acceptable coefficients of variation. The between-batch coefficient of variation was calculated for WES data at 3 and 7 days, the values were 0.56 and 3.13; the allowable is 10.7% for D2S%. No between batch coefficient of variation values could be calculated for the PSU data.

15.1.6 Between-Laboratory Coefficient of Variation

Since cracking of the PSU and WES samples affected their compressive strengths in different ways, calculating coefficients of variation for samples which are not highly similar may be misleading. However, it is possible to calculate values based on data collected prior to cracking. The 3, 7, and 28 day data are compared and results tabulated in Table 15.2. PSU data are compared with each SL batch at the same age, if appropriate.

According to C 109, the value of the coefficient of variation should not exceed 20.6%. The interlaboratory precision at these ages is well within ASTM specifications ranging from 9.0 to 15.7%.

Since varying degrees of cracking took place at later ages, the compressive strengths measured by the two laboratories at 56 and 90 days were quite different. The between-laboratories coefficients of variation for these two test times were 26.5 and 39.1%, respectively. However, again at 180 (181) and 365 days, both laboratories reported increases followed by decreases in strength and acceptable between-laboratory comparisons of coefficients of variation of

Table 15.2 Coefficient of Variation for PSU and WES Sample Data.

Time of Hydration	Calculation	C.V.,%
3 day	$\frac{7324-6290}{\frac{(7324+6290)}{2}} = \frac{1034}{6807} \times 100 =$	15.2
	$\frac{7324-6255}{\frac{(7324+6255)}{2}} = \frac{1069}{6790} \times 100 =$	15.7
7 day	$\frac{9459-8388}{\frac{(9459+8388)}{2}} = \frac{1071}{8924} \times 100 =$	12.0
	$\frac{9459-8129}{\frac{(9459+8129)}{2}} = \frac{1330}{8794} \times 100 =$	15.1
28 day	$\frac{13290-12150}{\frac{(13290+12150)}{2}} = \frac{1140}{12720} \times 100 =$	9.0

6.78 and 7.66, respectively. These values were not tabulated in Table 15.2 because of the observed cracking and resulting uncertainty in making these comparisons.

15.2 Young's Modulus

15.2.1 Static Modulus (PSU)

A static Young's Modulus was calculated using stress-strain data collected during compression testing of 2-in. (50.8-mm) cubes up to 365 days (Section 15.1). A tangent was drawn at approximately 40% peak height to extract the needed data. The results are presented in Table 15.3 and graphically in Figure 15.2. These measurements were made to explore the possibility of using these values as a possible source of verification of the dynamic modulus reported in Section 15.2.2 as well as to check the nature of the stress-strain relationships of the 2-in cubes during the compression test. Since a single data point was recorded at 180 days, its significance was open to question. For this reason it has been omitted from Figure 15.2.

Table 15.3 PSU Static Young's Modulus, Millions of psi.

3 day PSU #801667	7 day PSU #801644	28 day PSU #801665	56 day PSU #801668	90 day PSU #801666	180 day PSU #801669	365 day PSU #801670
0.889	1.043	1.239	1.471	1.168	1.214*	1.076
1.275	0.956	1.256	1.432	1.074		1.171
0.861	0.975	1.376	1.376	0.880		1.123
1.108	0.974	1.181	1.333	0.704		1.024
0.900	1.243	1.360	1.394	0.891		1.116
0.955	1.025	1.306	1.224	0.615		0.955
0.822	1.094	-	-	-		-
$\bar{x}$ = 0.981	$\bar{x}$ = 1.044	$\bar{x}$ = 1.286	$\bar{x}$ = 1.372	$\bar{x}$ = 0.889		$\bar{x}$ = 1.078
σ' = 0.154	σ' = 0.100	σ' = 0.075	σ' = 0.086	σ' = 0.211		σ' = 0.078

*Only a single value was obtained - equipment malfunction.

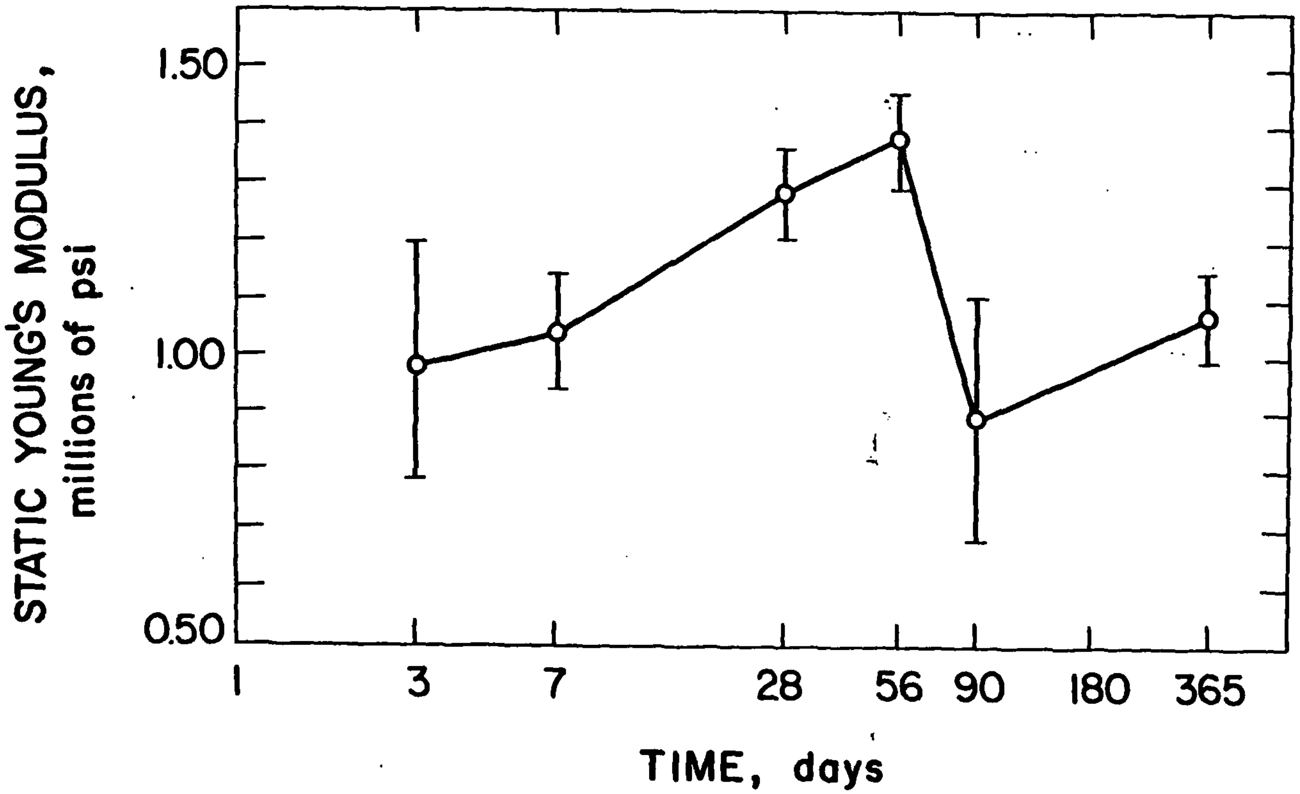

Fig. 15.2 Change in static modulus of elasticity with time.

15.2.2 Dynamic Modulus

Resonant frequencies were determined on demolding of bars and at 3, 10, 28, 56, 90, 180, and 365 days (WES), and at 2, 3, 7, 14, 28, 56, and 90 days age (PSU). Results are given in Tables 15.4 and 15.5, respectively, and shown in Figures 15.3 and 15.4.

15.2.3 Discussion

Trends shown by the modulus data in Figures 15.2 and 15.3 as a function of time may be compared with the plot of compressive strength versus time (Figure 15.1) which shows a similar trend. The departure of compressive strength (Figure 15.1) and the modulus data (Figures 15.2 and 15.3) from a straight line is the result of cracking of the unrestrained 2-in. (50.8-mm) cube specimens. However, development of the expansion on a straight line (see Section 15.5, Figure 15.6) indicates that restrain prevents the expansivity from degrading the mechanical behavior studied. For the dynamic E tests at WES the specimen was of 1-in (25.4-mm) cross section, but was unrestrained--each bar shows a slight reduction in E between readings after 28 days age (but the averages always show a slight increase). What this seems to mean is that the tendency to crack and degrade is nearly completely balanced by the tendency for mechanical property values to increase with time while moist curing is maintained. Presumably, had these specimens been restrained the E would have increased linearly with time. The values obtained by PSU at 60° and plotted in Figure 15.4 with WES data were obtained on three bars of different length, each having a 1-in. (25.4-mm) square cross section. Data for a single measurement made on a bar having dimensions of 1/2 by 1/2 by 4-in (12.7 by 12.7 by 101.6-mm) which was cured at 38°C for 14 days (frequency = 3760, mass (g) = 27.5, dynamic E = 2.77×10^6 psi) is also plotted. All bars were originally cast in 11-1/4-in. (285.8-mm) long molds and subsequently cut to size [4(101.6), 5(127), 8(203), and 10-in (254-mm)]. All measurements at PSU were made before the onset of major cracking at approximately 90 days (Figure 15.1) and therefore the plot of dynamic E versus time given in Figure 15.4 is nearly linear. A slight departure from linearity, a break in slope, can be inferred at 7 days. This may be due to actual mechanical changes in the sample in this time frame since these effects are also seen in

Table 15.4. WES 38°C Cured Resonant Frequency Test Results.

Specimen	Initial Reading			3 day	
	Frequency, Hz	Mass, lb	E*	Frequency, Hz	E*
(1) MD961-3	715	0.82	1.59	895	2.49
(2) MD962-1	740	0.85	1.765	930	2.79
(3) MD962-2	740	0.85	1.765	930	2.79
$\bar{x}$ =			1.71		2.69
σ' =			0.10		0.17
V,% =			5.92		6.44

Specimen	10 day		28 day	
	Frequency, Hz	E*	Frequency, Hz	E*
(1) MD961-3	945	2.77	1010	3.17
(2) MD962-1	980	3.095	1050	3.55
(3) MD962-2	995	3.191	1070	3.69
$\bar{x}$ =		3.02		3.47
σ' =		0.22		0.27
V,% =		7.31		7.75

Specimen	56 day		90 day	
	Frequency, Hz	E*	Frequency, Hz	E*
(1) MD961-3	1040	3.36	1030	3.30
(2) MD962-1	1050	3.52	1055	3.59
(3) MD962-2	1070	3.66	1080	3.76
$\bar{x}$ =		3.51		3.55
σ' =		0.15		0.23
V,% =		4.27		6.55

Specimen	180 day		365 day	
	Frequency, Hz	E*	Frequency, Hz	E*
(1) MD961-3	1035	3.33	1045	3.395
(2) MD962-1	1060	3.62	1080	3.76
(3) MD962-2	1080	3.76	1075	3.725
$\bar{x}$ =		3.57		3.63
σ' =		0.22		0.20
V,% =		6.14		5.55

*Dynamic Young's Modulus, millions of psi.

Table 15.5. PSU 60°C Cured Resonant Frequency Test Results.

Specimen	2 day			3 day		
	Frequency	Mass (lb)	Dynamic E*	Frequency	Mass (lb)	Dynamic E*
(1) 810286 (5-in.)	13771	0.390	3.88	13960	0.391	3.96
(2) 810286 (8-in.)	8692	0.623	3.91	8767	0.623	3.97
(3) 810286 (10-in.)	6948	0.768	3.84	6996	0.768	4.01
$\bar{x}$ =			3.88			3.98
σ' =			0.04			0.03
V,% =			0.91			0.66

Specimen	7 day			14 day		
	Frequency	Mass (lb)	Dynamic E*	Frequency	Mass (lb)	Dynamic E*
(1) 810286 (5-in.)	14296	0.391	4.16	14204	0.391	4.11
(2) 810286 (8-in.)	8946	0.624	4.14	8941	0.624	4.14
(3) 810286 (10-in.)	7111	0.769	4.03	7139	0.770	4.03
$\bar{x}$ =			4.11			4.09
σ' =			0.07			0.06
V,% =			1.70			1.39

Specimen	28 day			56 day		
	Frequency	Mass (lb)	Dynamic E*	Frequency	Mass (lb)	Dynamic E*
(1) 810286 (5-in.)	14422	0.392	4.24	14495	0.393	4.29
(2) 810286 (8-in.)	9000	0.625	4.20	9117	0.626	4.32
(3) 810286 (10-in.)	7217	0.771	4.16	7257	0.772	4.22
$\bar{x}$ =			4.20			4.28
σ' =			0.04			0.05
V,% =			0.95			1.20

Specimen	90 day		
	Frequency	Mass (lb)	Dynamic E*
(1) 810286 (5-in.)	14655	0.393	4.40
(2) 810286 (8-in.)	9212	0.627	4.42
(3) 810286 (10-in.)	7346	0.773	4.33
$\bar{x}$ =			4.38
σ' =			0.05
V,% =			1.07

*Dynamic Young's Modulus (millions of psi).

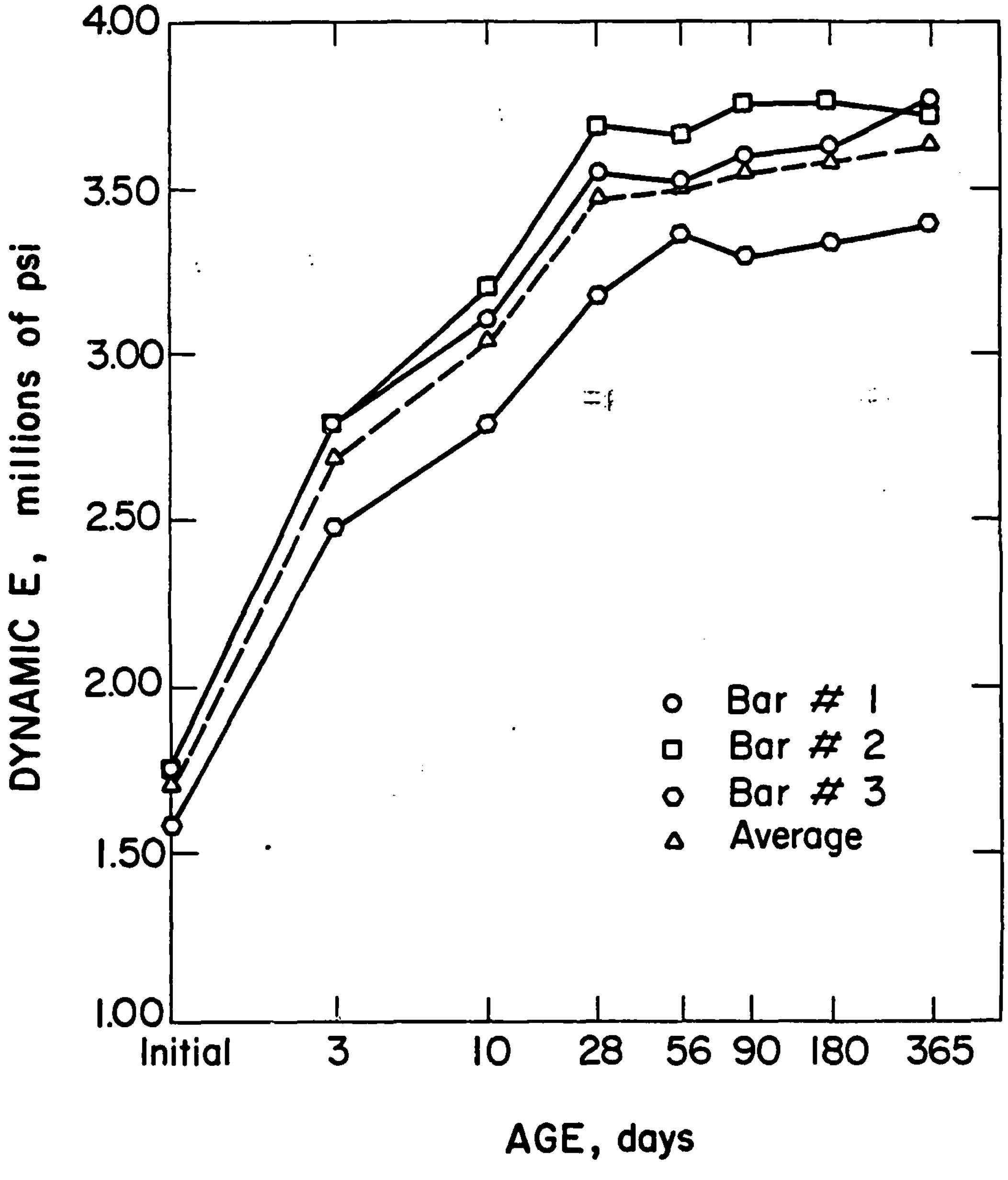

Figure 15.3. WES results for change in dynamic E with age.

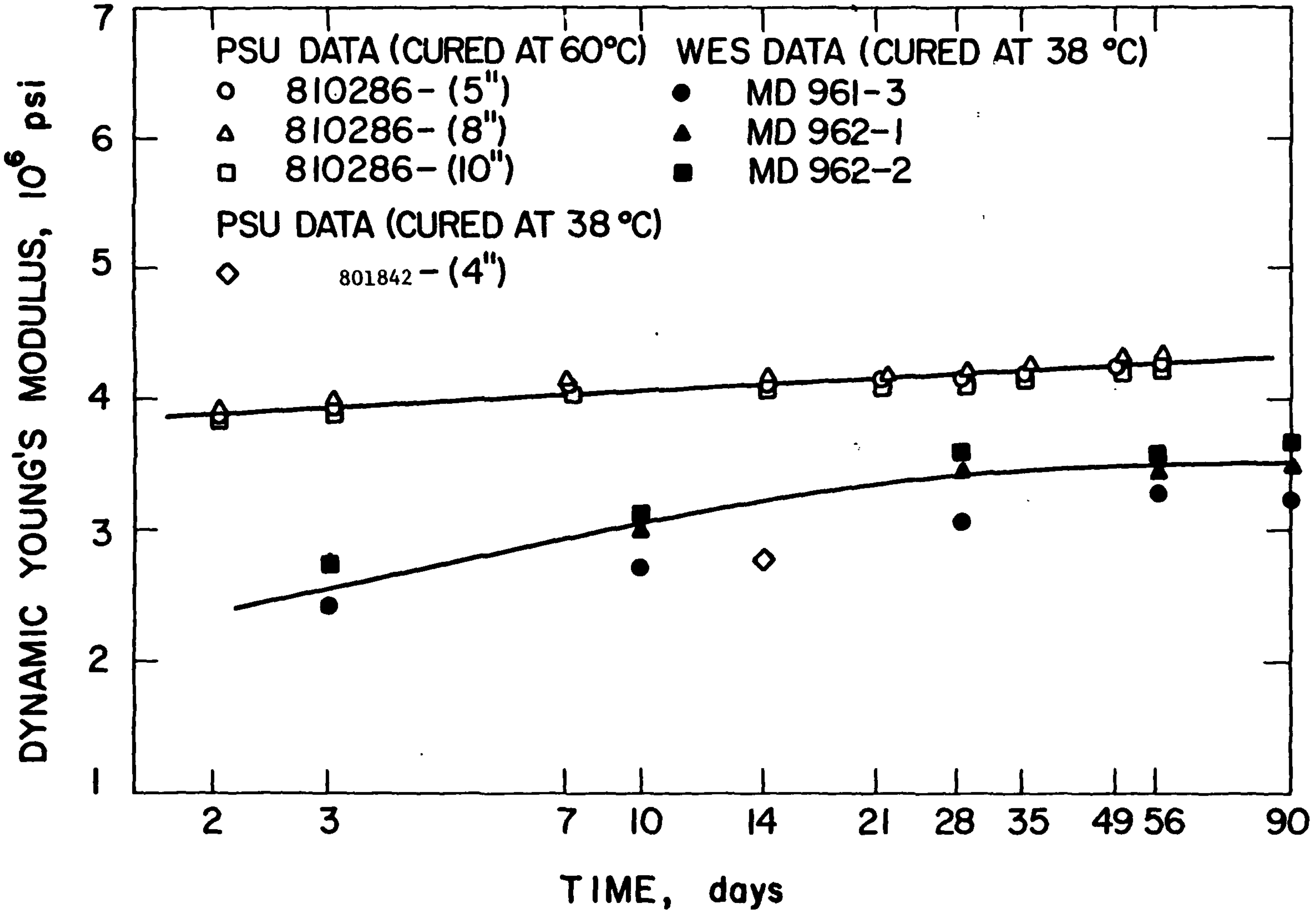

Figure 15.4. PSU and WES results for change in dynamic E with age.

other samples with different composition. This effect at 7 days is also noticeable in Figure 15.2 where the static modulus shows a slight departure from linearity when considering data to 56 days.

15.2.4 Within Laboratory Precision

No precision statements are given in ASTM C 215 for interlaboratory measurements, but satisfactory coefficients of variation are reported by both laboratories. The highest values reported by WES and PSU are 7.68 and 1.70% respectively. Since only a single measurement at the two laboratories was made at the same temperature (38°) but not at the same curing time (see Figure 15.4), it is difficult to make an interlaboratory comparison. However, since agreement between the single PSU data point and the WES modulus curve for the same time frame is within the range of error reported by WES for their three samples, the agreement of measurement between laboratories appears to be acceptable.

15.3 Density

15.3.1 WES - Density was determined on 2-in (50.8-mm) cube specimens upon demolding. The mass of the sample was determined after surface drying and again while immersed in deionized water. Results are given in Table 15.6.

15.3.2 PSU - Density was determined on each cube sample at 25 hr upon demolding as a check on sample reproducibility. Density was also determined prior to compression testing of cube specimens. Gross deviations from an average value or drastic changes in density during hydration would signal possible problems with a particular cube or set of cube specimens. Results are given in Table 15.7.

15.3.3 Results

The WES cubes involved six sets of three from one batch and five sets of three from a second batch. Data for within-batch and between-batch variation are presented in Table 15.6. Similar data for PSU measurements are presented in Table 15.7. Seven, 28, and 90-day data represent a single batch, while

Table 15.6. 24-hr Density of WES Cube Specimens, g/cm^3.

WES Batch #1

Set 1	2.061	Set 3	2.068	Set 5	2.068
	2.064		2.074		2.067
	2.069		2.082		2.068
$\bar{x}$ =	2.065	$\bar{x}$ =	2.075	$\bar{x}$ =	2.067
σ' =	0.054	σ' =	0.007	σ' =	0.001
V,% =	0.196	V,% =	0.338	V,% =	0.048
Set 2	2.054	Set 4	2.049	Set 6	2.067
	2.053		2.047		2.060
	2.058		2.056		2.073
$\bar{x}$ =	2.055	$\bar{x}$ =	2.051	$\bar{x}$ =	2.067
σ' =	0.0026	σ' =	0.005	σ' =	0.006
V,% =	0.129	V,% =	0.244	V,% =	0.290

Average, g/cm^3	2.0632
Std.Dev., g/cm^3	0.0092
Range, max.	2.082
min.	2.047
Difference	0.035

WES Batch #2

Set 1	2.062	Set 3	2.062	Set 5	2.074
	2.067		2.054		2.062
	2.070		2.063		2.058
$\bar{x}$ =	2.066	$\bar{x}$ =	2.060	$\bar{x}$ =	2.065
σ' =	2.004	σ' =	0.005	σ' =	0.008
V,% =	0.194	V,% =	0.239	V,% =	0.40
Set 2	2.054	Set 4	2.063	Average, g/cm^3	2.0645
	2.070		2.063	Std.Dev., g/cm^3	0.003
	2.073		2.072	Range, max.	2.074
				min.	2.054
$\bar{x}$ =	2.066	$\bar{x}$ =	2.066	Difference	0.020
σ' =	0.010	σ' =	0.005		
V,% =	0.49	V,% =	0.252		

Overall:		
	Average, g/cm^3	2.0639
	Std.Dev., g/cm^3	0.006
	Range, max.	2.082
	min.	2.047
	Difference	0.035

Table 15.7. Density of Cube Specimens, g/cm^3.

PSU #801667, Batch #2		PSU #801664, Batch #1		PSU #801665, Batch #1	
24-hr	3 days	24-hr	7 days	24-hr	28 days
2.094	2.093	2.090	2.088	2.094	2.104
2.091	2.098	2.089	2.093	2.092	2.111
2.092	2.090	2.091	2.093	2.094	2.106
2.096	2.097	2.087	2.094	2.096	2.114
2.096	2.100	2.087	2.090	2.078	2.100
2.098	2.103	2.087	2.096	2.087	2.106
2.093	2.095	2.092	2.097	2.108	2.125
$\bar{x}$ = 2.094	$\bar{x}$ = 2.100	$\bar{x}$ = 2.089	$\bar{x}$ = 2.093	$\bar{x}$ = 2.093	$\bar{x}$ = 2.109
σ' = 0.002	σ' = 0.004	σ' = 0.002	σ' = 0.003	σ' = 0.009	σ' = 0.008
(Δ = 0.006)		(Δ = 0.004)		(Δ = 0.016)	

PSU #801668, Batch #2		PSU #801666, Batch #1		PSU #801669, Batch #2	
24-hr	56 days	24-hr	90 days	24-hr	180 days
2.080	2.115	2.088	2.113	2.082	2.099
2.070	2.103	2.090	2.106	2.086	2.013
2.110	2.112	2.089	2.105	2.077	2.098
2.097	2.119	2.083	2.100	2.081	2.100
2.096		2.093	2.110	2.080	2.097
2.102	2.161	2.089	2.111	2.082	2.101
2.083	2.103	2.097	2.114	2.080	2.099
$\bar{x}$ = 2.091	$\bar{x}$ = 2.119	$\bar{x}$ = 2.090	$\bar{x}$ = 2.108	$\bar{x}$ = 2.081	$\bar{x}$ = 2.087
σ' = 0.014	σ' = 0.022	σ' = 0.004	σ' = 0.005	σ' = 0.003	σ' = 0.003
(Δ = 0.028)		(Δ = 0.018)		(Δ = 0.006)	

PSU #801670, Batch #2	
24-hr	365 days
2.092	2.099
2.084	2.088
2.087	2.093
2.083	2.085
2.082	2.090
2.094	2.097
2.077	2.087
$\bar{x}$ = 2.086	x = 2.091
σ' = 0.006	σ' = 0.005
(Δ = .005)	

24-hr density

Average Batch #1 = 2.091
σ = 0.002

Average Batch #2 = 2.088
σ = 0.006

Overall Average = 2.089
σ = 0.004

data for 3, 56, 180 and 365 days represent a second batch. Average densities of $\sim$2.06 g/cc and $\sim$2.09 g/cc were obtained at WES and PSU, respectively. The greater density revealed in the PSU data was caused by use of a grout consolidation procedure which was not used at WES (see Section 6.2.1). The greater density of the PSU specimens is associated with generally higher compressive strengths. Results of measurements at both laboratories are comparable. Overall coefficients of variation of WES and PSU are 0.29 and 0.19%, respectively.

15.3.4 Additional Density Measurements

In an attempt to understand the hydration process of a potentially expansive cementitious grout better, density measurements on each cube were made at PSU upon demolding at 24 hr and again just before testing. Comparative density data for each cube at 24 hr and just before testing are given in Table 15.7 and corresponding change in density (Δ) from 24 hr to time of test in Figure 15.5. The data show that the 24-hr densities for all samples are nearly the same (2.089 ± 0.004 g/cm^3). However, the increase in density (Δ) from 25 hr to the date of testing of a set of cube samples generally becomes larger as a function of time up to about 56 days; the maximum density change realized. The samples hydrate combining additional water and $Ca(OH)_2$ from the curing solutions, and increase in density. The 7-day density change is slightly lower than expected since the sample is not yet strong enough to resist the tendency to expand. Beyond 7 days, the cube is strong enough to resist the expansive forces and density changes increase until the onset of cracking beyond 56 days where the expansive forces exceed the tensile strength of the material.

15.4 Permeability

15.4.1 PSU Data - Permeability was measured on 2-in. (50.8-mm) diameter restrained cylindrical samples hydrated for 3, 7, 28, 56, 90, and 365 days. The heights of the samples were nominally one inch. Testing took place on samples which were poured into and cured in 2-in. (50.8-mm) ID stainless steel rings capped with 1/8-in. (32-mm) thick Teflon disk-shaped end-caps. Curing took place under saturated $Ca(OH)_2$ solution with end-caps in place. On testing, end-caps were removed, testing pressure was increased slowly in approximately 100-psi steps, starting at low pressures and checking for flow before going to higher pressures. The 3- through 365-day samples were impermeable to water for the stated pressure and time periods. Details are given in Table 15.8.

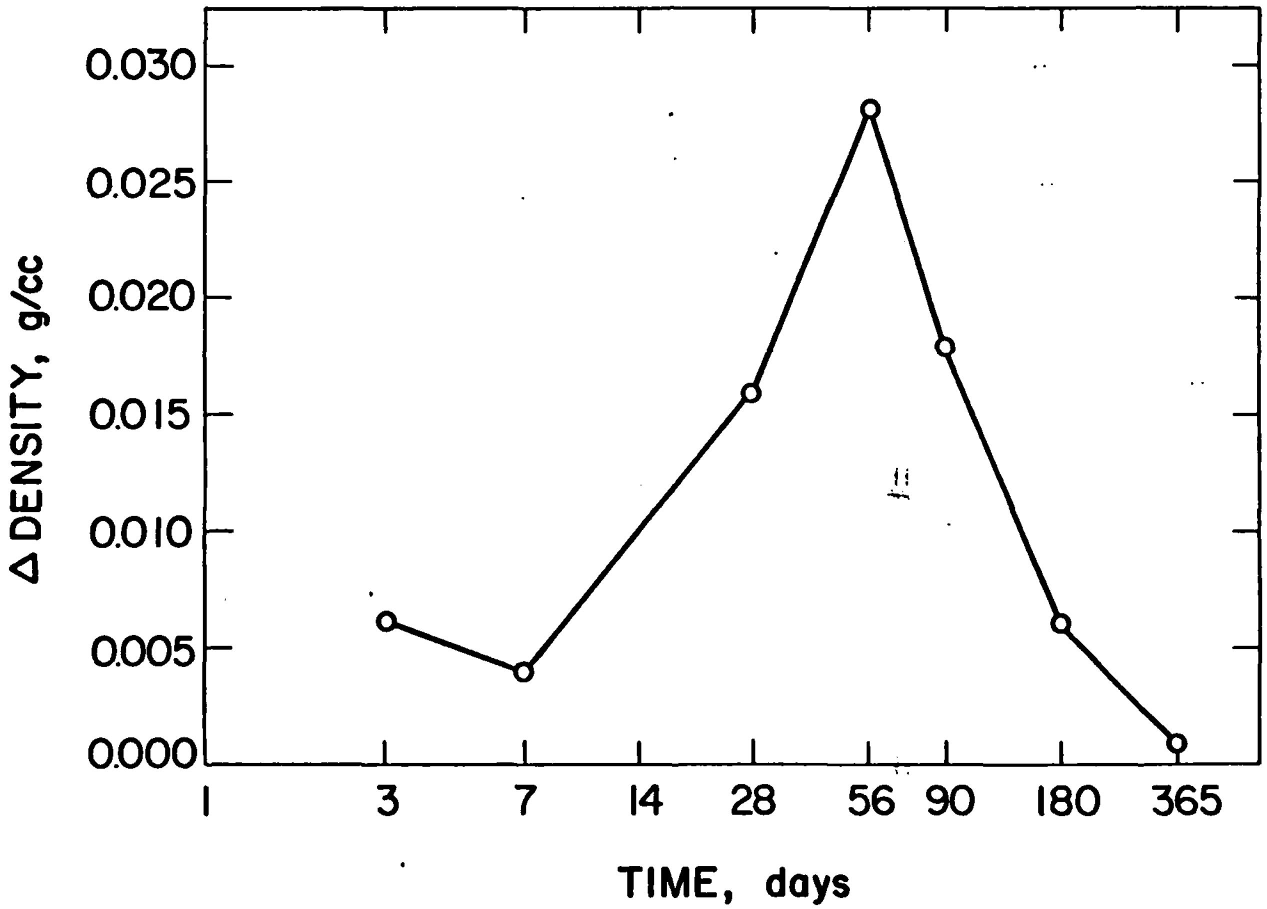

Fig. 15.5. Change in density (Δ) of 2-in (50.8-mm) cubes as a function of time.

To give numerical value to the term "impermeable," had 1-ml of water passed through the sample in the given time period, all permeabilities would have been in the 10^{-8} darcy range. Since no water passed through the samples the permeabilities are much less than 10^{-8} darcys. In addition, none of these restrained samples had cracked, although a slight dome-like thickening of the top and bottom of the samples was sometimes observed.

In addition to samples cast in stainless steel rings, permeability measurements were also made on approximately 1/2-in (12.7-mm) high cylindrical samples, cut and sealed with epoxy into ∿1-in. (25.4-mm) ID steel rings. Samples were either cast and cured in a sealed glass vial (semi-restrained) or molded for 24-hr in brass molds and then cured in saturated $Ca(OH)_2$ solution (unrestrained). Data for the glass vial cured samples given in Table 15.9 verify the general impermeability of the restrained samples tested above. The sealed glass vial samples are consistently impermeable. It was found in a companion study that the samples cured in a sealed environment such as a glass vial, did not produce as high an expansive force as did the solution cured samples, and therefore did not crack. However, effects of cracking were observed in cube specimens at 56 and 90 days in the compressive and modulus measurements (Fig. 15.1 and 15.2); the permeability of 1-in. (25.4-mm) unrestrained $Ca(OH)_2$ cured cylinder specimens show these same effects. They were impermeable to water under the time and pressures of the test through 28 days. At 56 days the sample cured in $Ca(OH)_2$ had a permeability of 9.7 x 10^{-5} darcys. Healing of expansion-induced cracks which was proposed to explain the regain of strength of the cube samples beyond 56 days also appears to be a viable explanation for the present phenomenon of regain of impermeability through 180 days. The 365-day sample had a pre-existing crack when tested. Flow rate was essentially linear through 20 hr which is equivalent to an apparent k of 1.8 x 10^{-6} darcys. Apparently, renewed cracking beyond 180 days was responsible for the measurable permeability.

15.4.2 WES Data

Two specimens were run at 8 and 29 days. The resulting permeability values for these samples were 6 x 10^{-8} and 2 x 10^{-7} darcys, respectively. These values indicate quite low permeability at both ages and do not necessarily indicate a change with increasing age.

Table 15.8. PSU Permeability of 2-in. (50.8-mm) Samples Cast and Cured at 38°C in Stainless Steel Rings.

	Height	pressure psi (Pa)	time interval hr	flow rate ml/sec	permeability* darcys
3 day	1.002-in.	91 (0.63)	0-50	none	$<2.0 \times 10^{-8}$
PSU #801651	(25.4-mm)	224 (1.55)	50-66	none	
		296 (2.04)	66-84	none	
		428 (2.95)	84-94	none	
7 day	1.016-in.	102 (0.70)	0-16	none	$<1.1 \times 10^{-8}$
PSU #801652	(25.2-mm)	200 (1.38)	16-24	none	
		303 (2.09)	25-47	none	
		404 (2.79)	45-163	none	
28 day	1.016-in.	105 (0.72)	0-50	none	$<1.2 \times 10^{-8}$
PSU #801653	(25.8-mm)	198 (1.37)	50-81	none	
		400 (2.76)	81-172	none	
56 day	1.087-in.	126 (0.87)	0-22	none	$<2.7 \times 10^{-8}$
PSU #801654	(27.6-mm)	112 (0.77)	22-46	none	
		310 (2.14)	46-69	none	
		404 (2.79)	69-71	none	
90 day	1.055-in.	110 (0.76)	0-20	none	$<5.4 \times 10^{-8}$
PSU #801660	(26.8-mm)	154 (1.06)	20-60	none	
		148 (1.02)	60-73	none	
365 day	1.055-in.	100 (.69)	0-05	none	$<8.8 \times 10^{-8}$
PSU #801657	(26.8-mm)	225 (1.55)	0.5-0.5	none	
		308 (2.13)	1.5-2.0	none	
		451 (3.11)	2.0-72	none	

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*calculated value assuming 1 mL had passed through the sample during the total time of the test under an average of the test pressures. Since there was no measurable flow, the actual permeability value is much less (<) than the value listed.

Table 15.9. PSU Permeability of Grout Samples Epoxied into Steel Rings after Curing in Either a Shell Vial or Saturated $Ca(OH)_2$ Solution, 38°C.

	3 day		7 day				28 day	
	cured in $Ca(OH)_2$	cured in shell vial	cured in $Ca(OH)_2$		cured in shell vial		cured in $Ca(OH)_2$	cured in shell vial
	PSU 801780	PSU 801795	PSU 801783		PSU 801796		PSU 801784	PSU 801798
pressure, psi (MPa)	500 (3.45)	500 (3.45)	500 (3.45)	1000 (6.90)	500 (3.45)	1000 (6.90)	1000 (6.90)	1000 (6.90)
time interval, hr	0-41	0-41	0-28.5	28.5-90	0-28.5	28.5-90	0-70	0-110.5
flow rate, mL/sec	no flow	no flow	no flow	some flow**	no flow	no flow	no flow	no flow
permeability, darcys	$<10^{-8}$*	$<10^{-8}$*	$<10^{-8}$*	---	$<10^{-8}$*		$<10^{-8}$*	$<10^{-8}$*

	56 day		90 day		180 day		365 day	
	cured in $Ca(OH)_2$	cured in shell vial	cured in $Ca(OH)_2$	cured in shell vial	cured in $Ca(OH)_2$	cured in shell vial	cured in $Ca(OH)_2$	cured in shell vial
	PSU 801786	PSU 801801	PSU 801788	PSU	PSU 801791	PSU	PSU 801792	PSU 801806
pressure, psi (MPa)	1000 (6.90)	1000 (6.90)	1000 (6.90)	---	1000 (6.90)	---	431 (2.97)	635 (4.38)
time interval, hr	0-137	0-137	0-119	---	0-192	---	0-20	20-68
flow rate, mL/sec	0.03	no flow	no flow	---	no flow	---	some flow***	no flow
permeability, darcys	9.7×10^{-5}	$<10^{-8}$*	$<10^{-8}$*	---	$<10^{-8}$*	---		$<10^{-8}$

*Less than (<) 10^{-8} darcy assuming less than 1-mL flow for the indicated time and pressure. See text.

**Epoxy may have leaked.

***Sample had a pre-existing crack when tested. Flow was essentially linear through 20 hr which is equivalent to an apparent k of 1.8×10^{-6} darcys. When the pressure was raised to 635 psi (4.38 MPa), the sample failed.

15.4.3 Between-Laboratory Comparison

All of the values for permeability obtained in both laboratories indicate similar results, i.e., virtually no flow, depending upon age and curing condition of the sample.

15.5 Expansion

15.5.1 WES Restrained Expansion

Results obtained by WES for ages of 1, 3, 7, 28, 56, 116, 176, 236, and 365 days are presented in Table 15.10. The trend in volume change data shows that increasing expansion occurs with time for each bar; expansions were similar for the two bars. Figure 15.6 shows that the measured expansion follows an approximate straight line on a log-time plot. This indicates that the departure of the cube strength change with time (on a log scale) (Figure 15.1) represents a tendency to self-destruction of unrestrained expanding specimens--a process that can be precluded by providing restraint. It also suggests that the expansive tendency continues to develop over time in a moist environment, but at a decreasing rate.

15.5.2 PSU Early Dimensional Change

Bulk volume change measurements at room temperature were made comparing the basic mixture (1) using deionized water and (2) deionized water with supplemental $CaSO_4 \cdot 2H_2O$ added as mixing water for the grout. Mixtures were prepared by API mixing procedure. In this measurement, (1) volume shrinkage was observed up to 21 hr with deionized water, reaching a maximum of 1.3%, then followed by expansion. The maximum shrinkage in (2) was larger and was delayed to 26 hr, reaching ∿1.9%, followed by slight expansion. Experiments were terminated at ∿38 hr.

Longitudinal dimensional change measurements (at room temperature) were also made on the Table 4.1a (Section 4.3) final mixture. This measurement started at about 6 hr after mixing; the time at which the specimen would support the measuring plunger. Figure 15.7 shows the cumulative longitudinal shrinkage up to ∿26 hr (∿0.073%) followed by expansion, reaching a net positive linear expansion of 0.05% at 120 hr, the end of the test. The volume and linear measurements are not strictly comparable because of the restraint of the mold in the latter case, despite its lubrication.

Table 15.10
Restrained Expansion of Bars Cured at 23°C for 24 hr, and Stored at 38°C

Age	Bar 1*	Length Change**	Bar 2*	Length Change**	Length Change Percent	σ, in.	V Percent
Bar before molding	0.0856	--	0.1050	--	--	--	--
24 hr	0.0951	0.0095	0.1144	0.0094	0.094	0.0001	0.75
3 day	0.0989	0.0133	0.1183	0.0133	0.133	0.0000	0.00
7 day	0.1038	0.0182	0.1234	0.0184	0.183	0.0001	0.73
28 day	0.1103	0.0247	0.1293	0.0243	0.245	0.0003	1.15
56 day	0.1128	0.0272	0.1320	0.0270	0.271	0.0001	0.52
116 day	0.1154	0.0298	0.1355	0.0305	0.302	0.0005	1.64
176 day	0.1189	0.0333	0.1379	0.0329	0.331	0.0003	0.85
236 day	0.1222	0.0366	0.1414	0.0364	0.365	0.0001	0.39
[illegible] day	0.1246	0.0390	0.1443	0.0393	0.392	0.0002	0.54

* Difference in length of restraining rod and reference bar, in.

** Change in length of restraining rod, in.

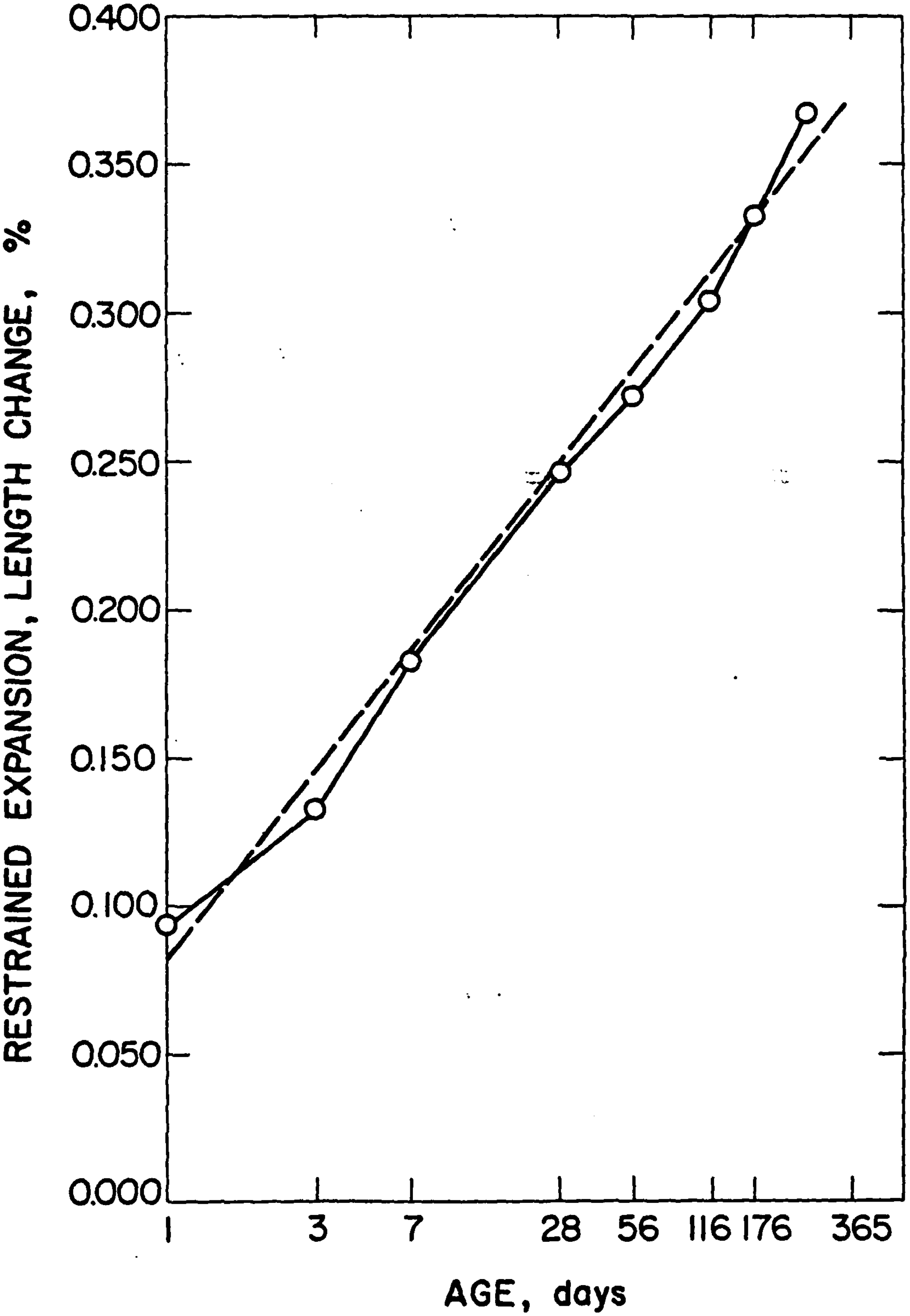


Fig. 15.6 Restrained expansion.

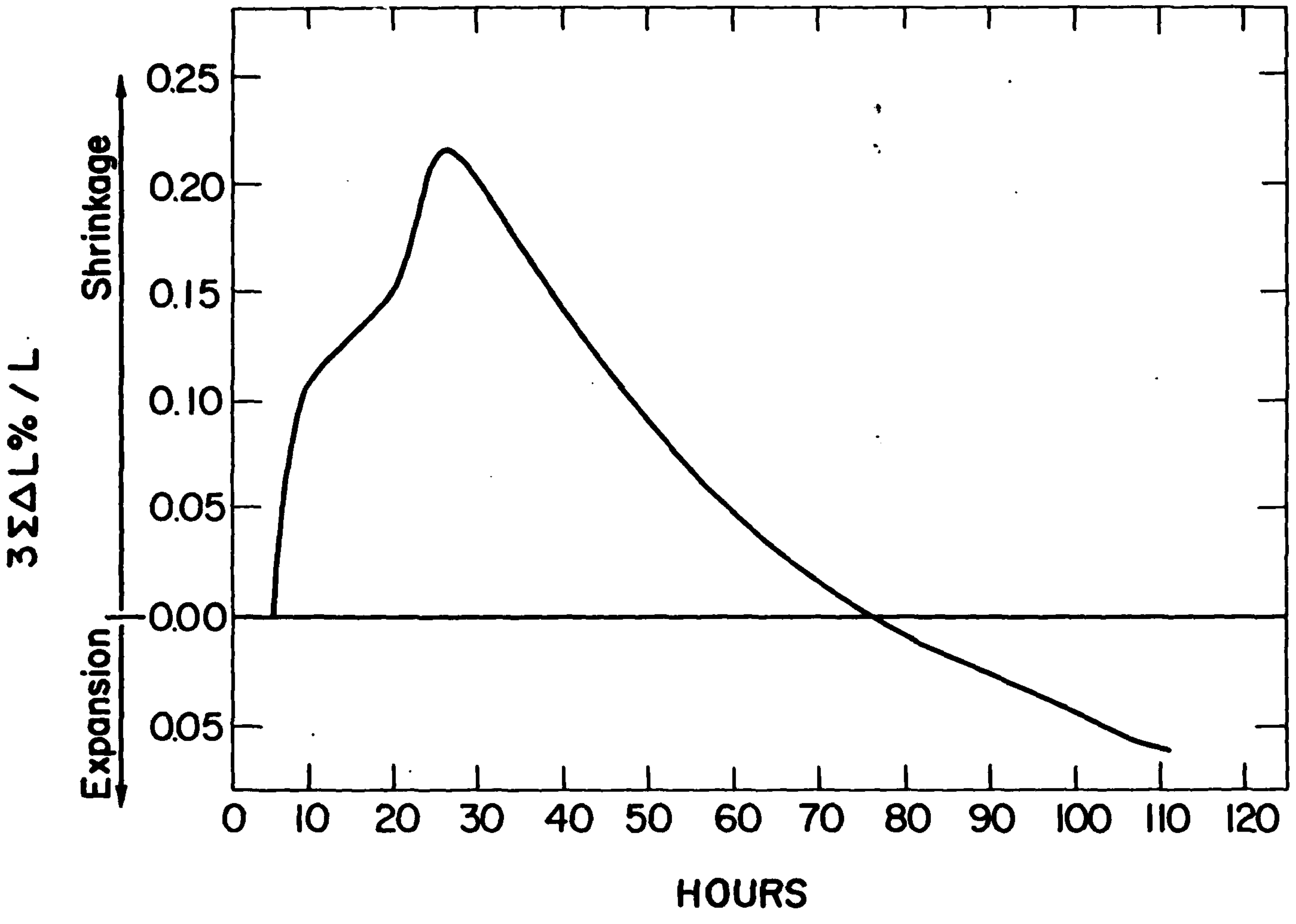


Fig. 15.7. Linear (longitudinal) dimensional change of fresh water mixture (Table 4.1a) at ∿23°C between 6 and 120 hr.

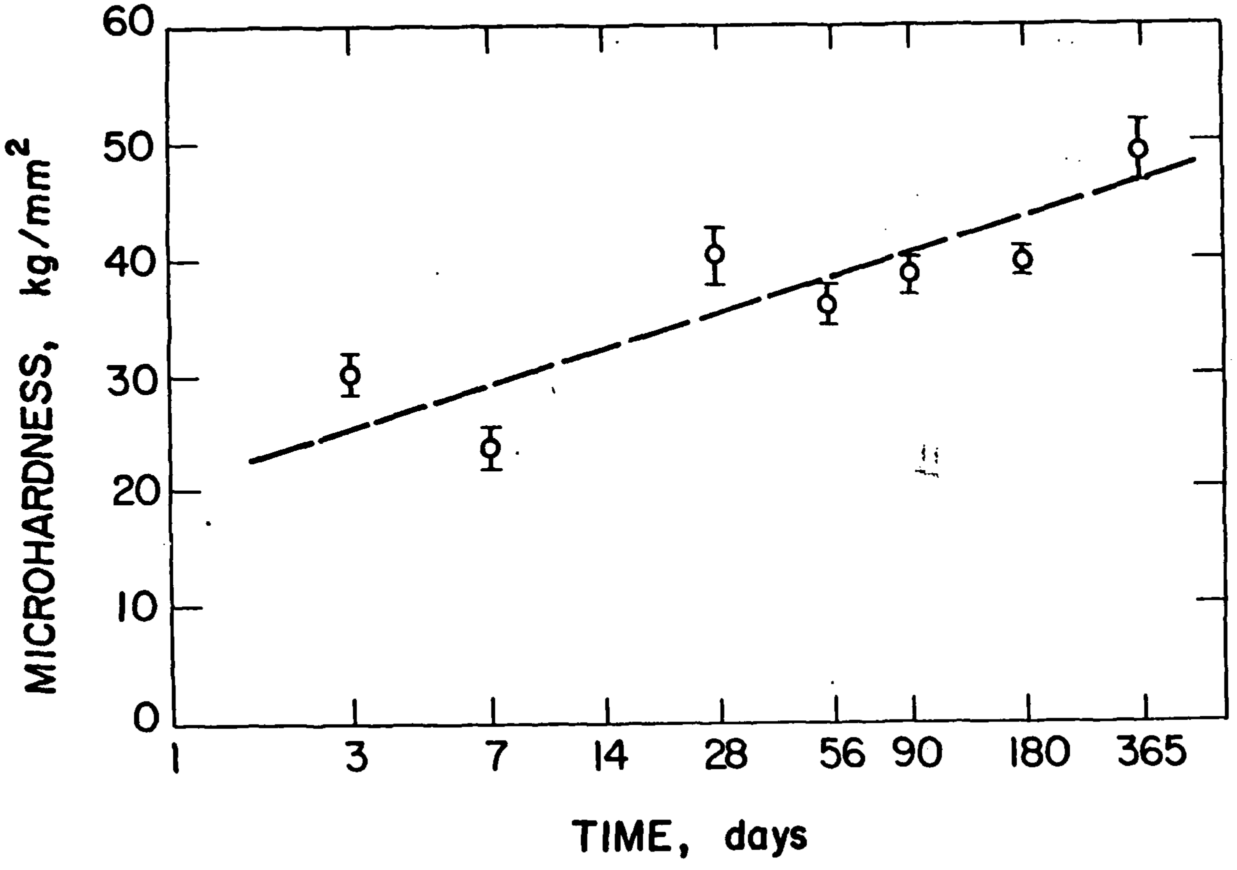


Fig. 15.8 Microhardness of grout as a function of time.

15.6 Microhardness

Microhardness measurements were made on disks of shell vial cured grout samples as a function of time. These data are summarized in Figure 15.8. Microhardness is a measure of the resistance of a given material to penetration by a Vickers diamond indentor. In part it measures the resistance to crushing or densification, and in part the tensile strength of the tested material. It is not as sensitive to the mechanical state of the total sample as is the compressive strength test, but more nearly reflects the state of the paste matrix itself. These data indicate that this mechanical property of the paste matrix increases as a function of time. It complements the other measurements, and affirms the satisfactory nature of the mixture, since the ultimate use of the expansive grout would be in the restrained condition under which the samples also have very high strength.

16.0 Other Characterization

16.1 Scanning Electron Microscopy

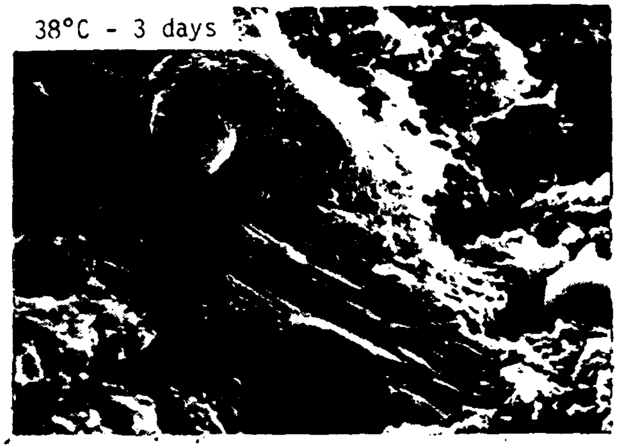
Scanning electron microscopy (SEM) studies of hydrated grout specimens stored in sealed vials for 3, 7, 28, 56, 90, and 180 days were performed at PSU and at 3, 29, and 365 days at WES. The intent of the study was to compare results of observed surface detail using each institution's SEM to examine comparably hydrated samples. In addition to narrative results, SEM images of representative areas were also presented as a series of figures. Whenever possible both laboratories tried to furnish photographs at ∿1000X and ∿5000X to make the comparison somewhat easier. The option of including additional SEM images for each age allowed each laboratory the option of including additional material having relevance to the subject matter being presented.

16.1.1 PSU - Specimens were fragmented by breaking or reduced to suitable size with a diamond saw prior to examination. They were either run in the "as-cured" condition on the day they were removed from the curing chamber, or suitably freeze dried for examination at a later date. Samples were sputter coated with a gold film to insure conductivity of the sample.

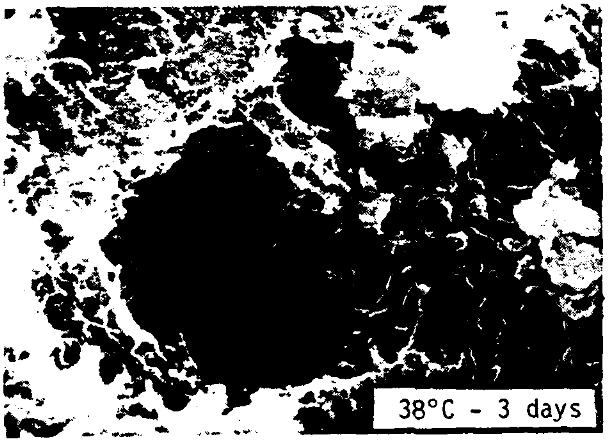
SEM images of shell-vial cured samples are presented as a series of figures (16.1 - 16.6). Each figure consists of a low and moderate magnified image (views a and b, respectively) showing typical areas of cured paste. View c generally is a higher magnification image intended to illustrate a particular point of interest. Results of general observations are given below.

Prisms or needles of ettringite were most commonly observed having grown in pockets or void spaces in the cured grout samples. These were most easily located in the youngest samples and were clearly evident at 3, 7, and 28 days. At ages beyond 56 days, with increasing completeness of hydration, these occurrences became scarcer, although prisms could be found with increasing difficulty (see for example Figures 16.4 and 16.5--56 and 90-day results, respectively). At 180 days no ettringite having this particular morphology was found. At 180 days, however, in view c (lower left-hand corner) one does see ettringite-like material, but it is of a more massive habit. This latter massive material may be the more common form of ettringite. It is more difficult to recognize, but may be responsible for the abundance of ettringite in the x-ray diffraction pattern.

Figure 16.1 SEM images of 3-day "as-cured" shell-vial cured samples.



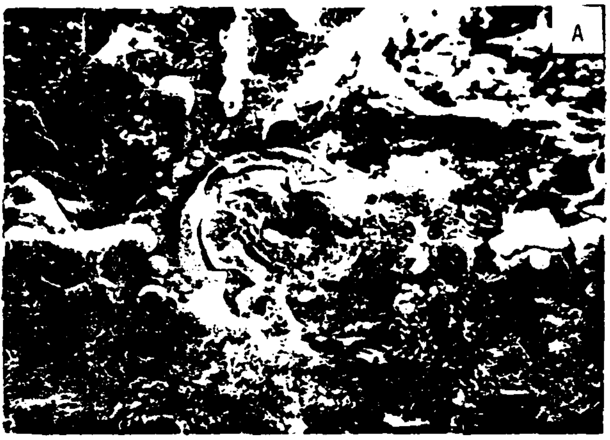
a) Overall view of typical surface at 1060X showing massive $Ca(OH)_2$, fly ash spheres and voids.



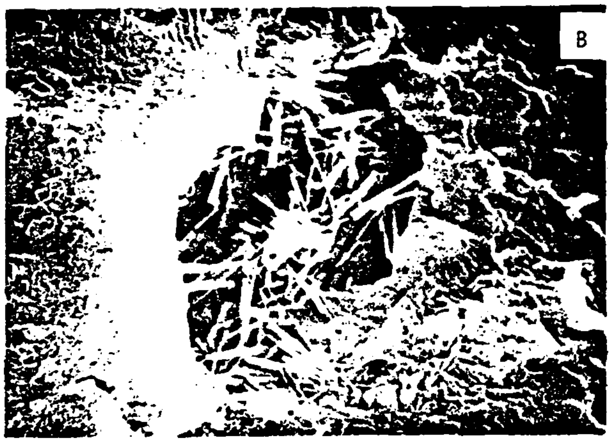
b) Ettringite and C-S-H matrix detail (5050X).

c) Enlargement of ettringite crystals showing hexagonal cross section (30700X).

Figure 16.2 SEM images of 7-day cured 60°C vacuum dried shell-vial samples.



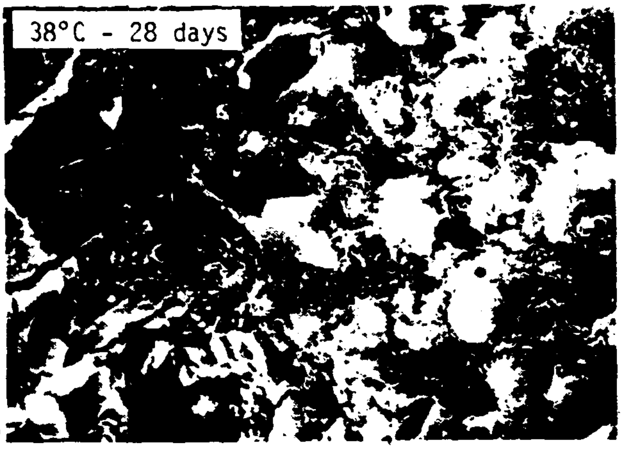
a) Overall view of typical surface at 1060X showing fly ash spheres, fly ash voids and dense matrix. A collapsed fly ash shell with internal crystallites is visible.



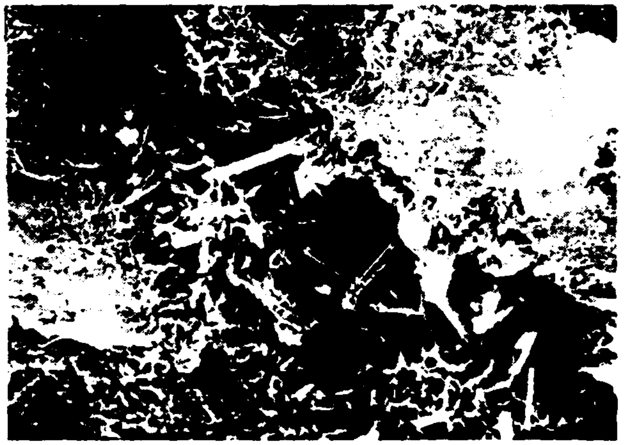
b) Ettringite detail growing in two hexagonal $Ca(OH)_2$ casts and dense matrix material (5050X).

c) Ettringite growing in a void space surrounded by C-S-H type matrix material (5050X).

Figure 16.3 SEM images of 28-day cured shell-vial samples.



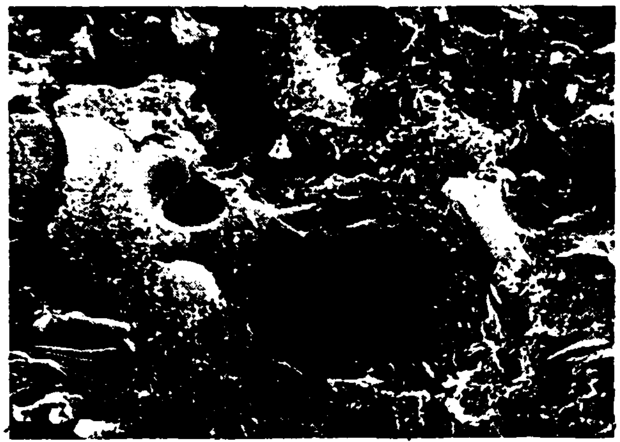
a) Overall view of typical surface of "as-cured" sample at 1060X showing reacted fly ash spheres and pockets of ettringite in a massive matrix.



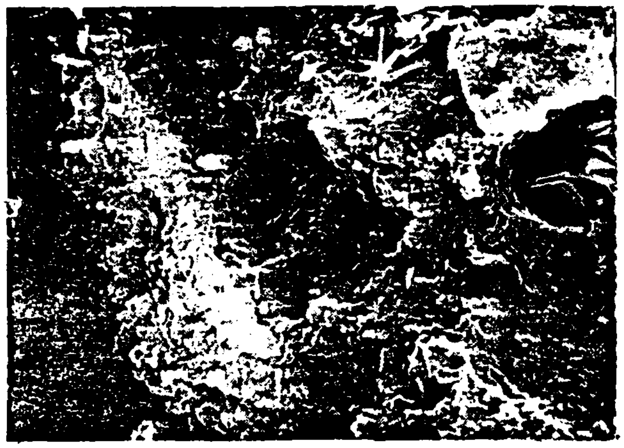
b) Ettringite detail in one such pocket from cement micrograph a (5050X).

c) Fly ash detail showing glass sphere in process of hydrating (19600X).

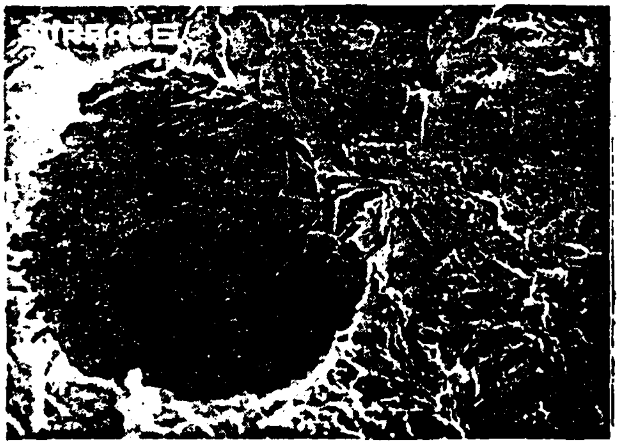
Figure 16.4 SEM images of 56-day "as-cured" shell-vial cured samples.



a) Overall view of typical surface at 1490X showing partially hydrated fly ash spheres in cross section, some minor ettringite, massive $Ca(OH)_2$ and a dense matrix.

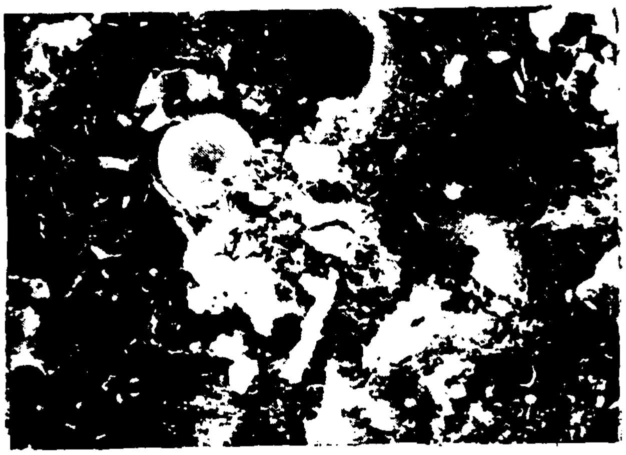


b) Ettringite and matrix detail. Ettringite was difficult to find in this void-filling morphology (2910X).

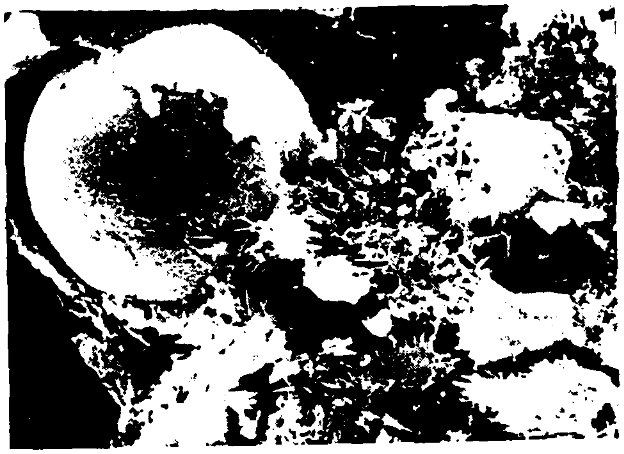


c) Detail of inside and outside of a glassy fly-ash sphere in partial state of hydration. External platy growth as well as blade-like structure of the hydrated material adjacent to the fly-ash sphere are typical features (10000X).

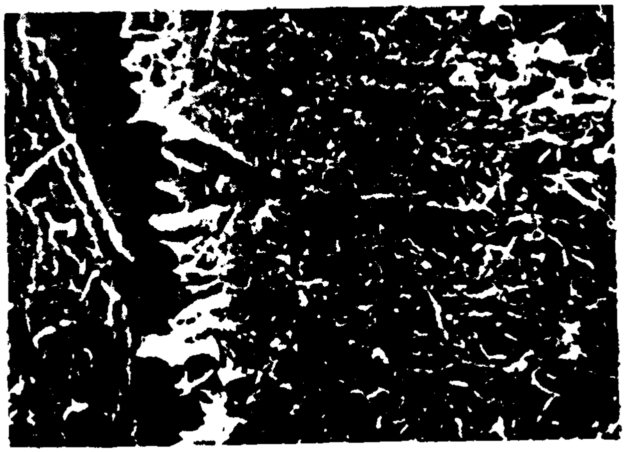
Figure 16.5 SEM images of 90-day "as-cured" shell-vial cured samples.



a) Overall view of typical surface at 1050X showing fly-ash spheres and voids in various states of hydration. Some ettringite in pockets and massive matrix is also evident.

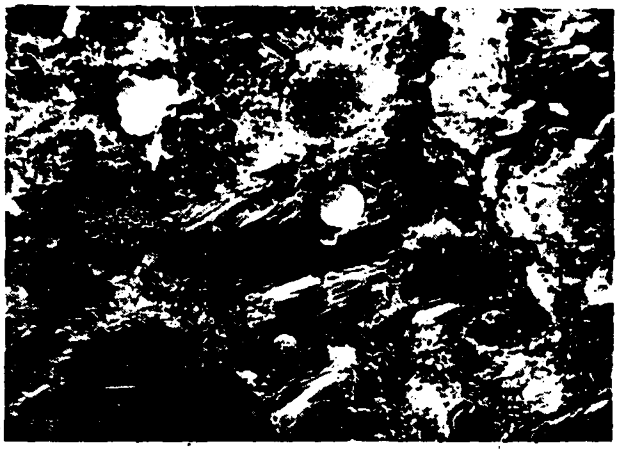


b) Detail of fly ash and ettringite (3070X).

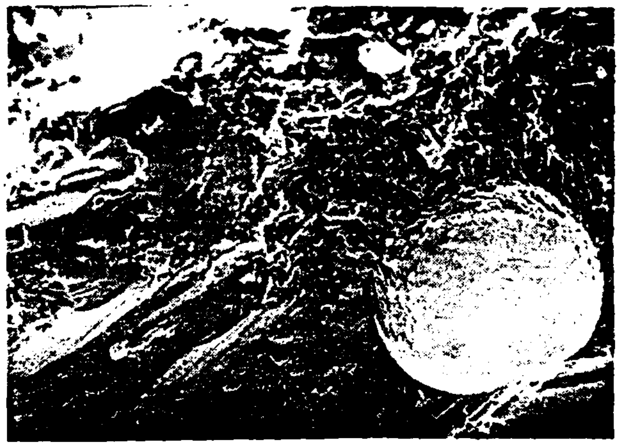


c) Detail of fly ash/matrix contact.Fly-ash sphere surface is on left. Blade-like crystals in center of photograph are typical hydration products of the glassy fly-ash sphere (30700X).

Figure 16.6 SEM Images of 180-day cured freeze dried shell vial samples.



a) Overall view of typical dense surface at 1000X showing fly-ash spheres and voids in various states of hydration. Also shown are massive $Ca(OH)_2$ and dense matrix material.



b) Detail of fly ash, $Ca(OH)_2$ and matrix material. The hydrated material surrounding the fly ash has a typical blade-like structure (4810X).

c) Detail of fly-ash surfaces with neighboring blade-like crystals and matrix material (7610X).

Fly ash spheres in various states of alteration were observed throughout the 365-day curing of the paste. Smooth, glass-like sphere surfaces were more apparent in the earlier samples, becoming progressively more reacted with increasing curing time. The glassy sphere begins to react from the outside and if fluid can enter into the sphere through cracks or imperfections, hydration begins on the inside of the sphere as well. The hydration of the fly-ash sphere is such that a weak bond is formed between the glass and its nearest hydration product. Thus early samples had a dearth of sphere-void combinations where part of the sphere had hydrated and the central glassy portion had been pulled out leaving a hydrated void behind. The sphere was commonly smooth with some larger blade-like crystals adhering to its surface. As a rule, the voids are not smooth, but fairly intricate structures consisting of honey-comb or geometrically consistent networks of blade-like crystals (the same as are found on the surface of the fly-ash spheres). These features, which are due to pull out of a fly-ash sphere, are gradually replaced by cross-sectional views of completely or partially hydrated fly-ash spheres with hydration products both inside and outside of the rims of remnant glass spheres.

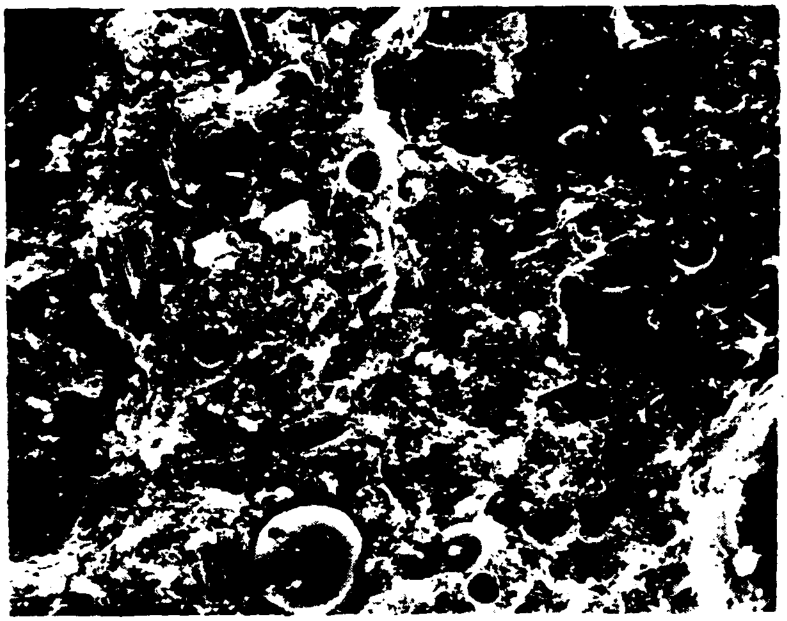
Calcium hydroxide can be found at all ages of paste hydration. The hexagonal-plate crystal habit is most common at the earliest ages. Hexagonal void spaces present at earliest times tend to suggest the former presence of hexagonal plates of $Ca(OH)_2$. At later ages of hydration only massive $Ca(OH)_2$ is observable. These massive deposits are often associated with fly-ash spheres.

Densification of the paste with time seems to be occurring. Pockets of ettringite are being filled or replaced by other material. Fly ash spheres are hydrating and becoming part of the matrix material. In broken samples the fly ash spheres act as centers of weakness and therefore are involved in the breaking process, the glass-to-hydration product rims being a weak link in the younger pastes. In older pastes the fly-ash spheres are hydrated and incorporated into the matrix, becoming less involved with the breaking process. If hydrated samples of cured paste are cut with a diamond saw and examined, one is impressed with the lack of void features which are so common in broken samples. Cross sections of fly-ash spheres show hydration in various stages, and that the hydration rim is continuous from the glass surface to the matrix. There is very little evidence to indicate a gap of any kind between glass spheres and hydration rim. The matrix is very dense and the actual void features attributed to the presence of fly-ash spheres are few.

16.1.2 WES - It was planned to examine microstructure by scanning electron microscopy (SEM) at 3-, 28-, and 365-day ages. Since the SEM was not in operation when the grout was three days old the specimen was prepared and stored in a desiccator over silica gel for an additional 59 days. Another three-day-old x-ray sample which had been stored in methanol in a freezer was also prepared and examined as an SEM sample at this time. Examination of this x-ray sample after it had been in cold storage for 21 days had showed that no additional hydration had occurred. In fact, both specimens were examined at the same age after different storage. The results agreed with other experimentation in this laboratory that has indicated that this storage in methanol effectively stops hydration. Thus, the presumption was that the two specimens that had been in storage for 59 days were still as they had been at 3 days age.

Data for 3-, 28-, and 365-days sealed vial samples are given in Figures 16.7 through 16.10. Comparison of micrographs 112480-5 (desiccator) and 112480-20 (methanol) with micrograph 102480-27 indicates normal microstructure of a hydrated cement mixture at these 3- and 29-day ages. The nominal 3-day-old grout (micrographs 112480-5, 2, 20, 18) showed unhydrated cement grains, fly-ash spheres, and hydration products and with *significant void space*. The 29-day-old grout (micrographs 102480-27, 25) showed more hydration products and less void space. Micrographs 092481-17 and 21 in Figure 16.10 show this grout at an age of 365 days. The structure is dense and unhydrated cement is still evident.

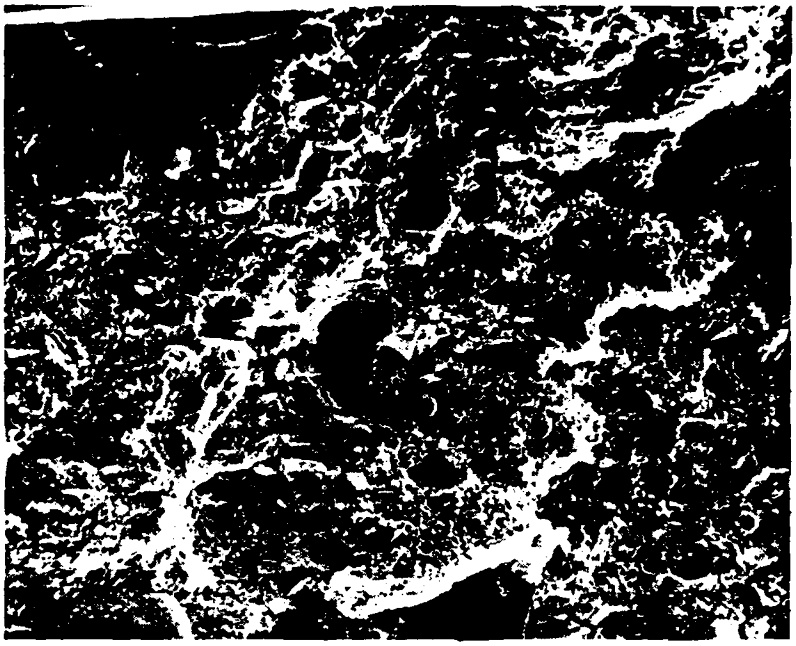
Figure 16.7 SEM images of 3-day cured sealed vial samples stored in a desiccator.



Micrograph 112480-5 of nominal 3-day old hydrated grout mixture, 1000X. Residual cement grains, fly-ash spheres, and hydration products are visible, with void space characteristic of young paste.

Micrograph 112480-2, 5000X. Enlargement of central portion of above micrograph.

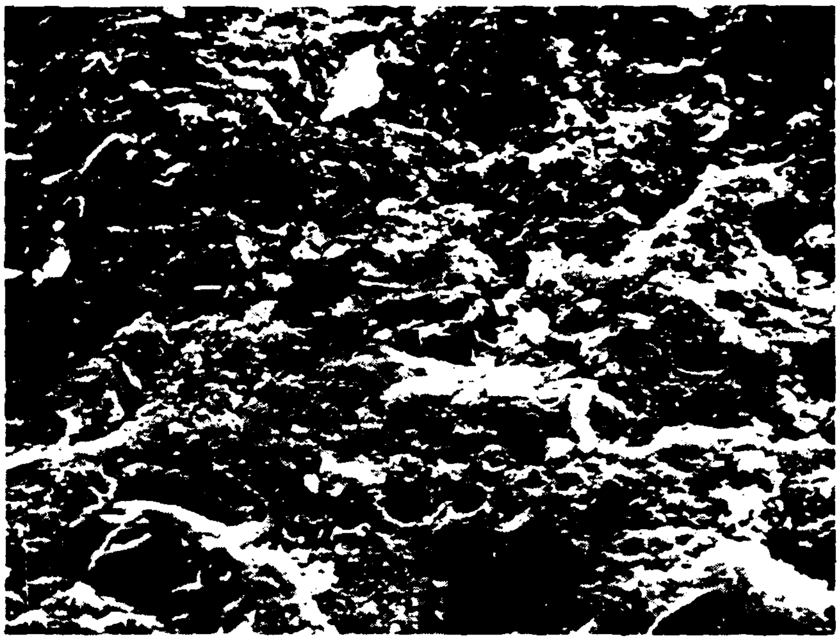
Figure 16.8 SEM images of 3-day cured sealed vial samples stored frozen in methanol.



Micrograph 112480-20 of nominal 3-day hydrated grout, 1050X. Similar to micrograph 112480-5.

Micrograph 112480-18, 5250X. Enlargement of central portion of above micrograph.

Figure 16.9 SEM images of 29-day cured sealed vial samples.



Micrograph 102480-27 of 29-day old hydrated grout mixture, 1000X. The microstructure is significantly denser than that at the earlier ages (micrographs 112480-5 and 20).

Micrograph 102480-25, 5000X. Enlargement of void near center of above micrograph. Abundant calcium hydroxide and needles or rolled foils are present.

Figure 16.10 SEM images of 365-day cured sealed vial samples.

Micrograph 092481-17 of 365-day-old hydrated grout mixture, ~1000X. Dense microstructure with residual cement grain near center.

Micrograph 092481-21. Same as above, but in different area. Lower left is partially hydrated cement grain, ~5000X.

17.0 Discussion and Conclusions

The present study has involved an interlaboratory comparison of methodologies used in investigating repository seal materials. The study involved selection of a specific cementitious material mixture with potential application as a borehole plugging material in anhydrite, halite, or adjacent members of an evaporite repository formation. The emphasis was on a comparison of test methods and research methodologies used to select the materials and mixture proportions and evaluate those properties that are relevant to potential long-term geologic repository performance in a specific geochemical environment.

The two laboratories began from different starting points, experience, and emphases. The PSU Materials Research Laboratory has a primary research and development commitment in characterization and properties which has led it to a secondary involvement with standardized methods and tests. The characterization and properties studies require precision and reproducibility of results. Methodology newly generated in this pursuit then develops standardized procedures in its maturity. The Structures Laboratory (SL) of the Waterways Experiment Station in the parts concerned with concrete, hydraulic binders, pozzolans, and other mineral admixtures, also had an original commitment to development of basic research data on materials characterization and behavior. It has also long been dedicated to standardized test methods to assess properties of materials. These commitments evolved so that the SL is now well equipped both for characterization of materials and development and use of standardized tests. The differences in approach and methods between laboratories were resolved by agreement on a test cementitious grout mixture, whose proportions were selected by PSU and modified at SL. Following this, experiments and tests were performed, in both laboratories to complete the final selection of the mixture proportions. It was agreed that certain tests would be performed in both laboratories to provide a comparison of numerical results obtained with similar procedures, and also that each laboratory would perform some studies or tests not done by the other, in order to provide supplemental information on certain performance-related materials, properties, or characteristics.

There is generally good agreement between the results of the tests that were performed by both laboratories, which provides confidence in the ability to reproduce the results of tests and methodologies. Starting materials were found to be highly similar when received from a common source, which in other circumstances often was not the case. Reproducibility was enhanced by the fact that certain of the materials were received by SL, the lots split and part transshipped for PSU. There is also the added accomplishment that when non-identical methods were used to formulate the grout or to study the starting materials and the cured grout, complementary types of information were obtained. There was further general agreement in interpretation of the meaning of observations.

Since the grout under study is a candidate material for use as a repository seal material in boreholes were post-placement consolidating effort will not, and cannot, be supplied, the grout must normally be effectively self-consolidating. Standard procedures for specimen making that involve post-placement compaction or consolidating effort should be modified to omit such steps, since the study demonstrated that the effects of consolidation were small and not apparently significant over the long term. For other areas where consolidation is feasible, such as in larger structures, in tunnels or shafts, where the grout would form the matrix of concrete, this modification would not be necessary.

Generation and comparison of quantitative data for the grout at later ages up to 365 days by the two laboratories has verified the earlier conclusion, stated in ONWI-198 that both obtain results that are in good agreement.

Compressive strength, Young's modulus, 24-hr density and permeability measurements, even when not in total agreement, all demonstrated trends which were very similar from laboratory to laboratory.

Phase identification by x-ray diffraction showed good agreement between the two laboratories, and detailed comparison of x-ray diffraction patterns by peak positions and intensities in Tables 14.2 through 14.8 show excellent agreement; the major spread in peak position was 0.14 Å for the 9.7 Å peak of ettringite; this would pose no problem in knowing that both laboratories identified the same peak, which is the criterion that is properly considered. There was more spread in peak intensities, but this is not considered serious since several factors other than the amount of constitutent present may influence peak intensity. Identification of the same x-ray diffraction peaks by the two labs in Table 14.9 show good agreement. The fact that agreement is not as good as in Table 14.10 in relation to minor peaks can be explained by the fact that the WES procedure is designed to delineate more clearly weak x-ray diffraction peaks while the PSU procedure does not put as much emphasis on weak peaks. Bearing this difference in emphasis in mind the agreement in Table 14.10 is satisfactory and could be improved as needed by even more detailed studies.

While it is not possible to make quantitative comparisons regarding the two sets of scanning electron micrographs made by the two laboratories, it is clear that both are illustrating similar microstructures, sequences of phase changes, and making similar interpretations.

Considering the quantitative data, the qualitative data, and the statistical comparisons of data, it can be concluded that both laboratories are producing data that are in good agreement. These data show the grout mixture studied at the two laboratories has proper physical properties, phase compositions, and microstructures for the materials used and ages covered.

Finally, the study demonstrated that an in-depth study of this type could lead to confirmation that the selected proportions for an experimental grout mixture would be satisfactory from a broader range of considerations, both relating to early-stage performance, and having implications for longevity in performance.

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19.0 Personnel and Acknowledgments

Dr. D.M. Roy is the principal investigator for the PSU repository seal materials investigations. Work at PSU was under the general guidance of Drs. D.M. Roy and M.W. Grutzeck. Dr. P.H. Licastro supervised some operations. Chemical analyses were performed by PSU's Mineral Constitution Laboratory. Other characterization and test data reported were performed by: A. Kumar - density, compressive tests, Young's modulus, mixing, viscosity; K. Owaga - density, air-permeability fineness; E. White - air-permeability fineness, wet-sieve tests, viscosity; L. Wakeley - x-ray diffraction; D. Wolfe-Confer - compressive tests, specific gravity, mixing procedures; A. Rousan - early heat of hydration; S. Goto - zeta potential; M. Grutzeck - permeability, viscosity, scanning electron microscopy; B. Scheetz - scanning electron microscopy; M. Perez - early dimensional change; M. Gharib, Young's modulus; Z. Chang - Young's modulus.

Work at WES was under the general direction of Bryant Mather, Chief, Structures Laboratory (SL). Katharine Mather is the principal investigator for the Geochemical Program at the SL. J.M. Scanlon, Chief, Concrete Technology Division, SL, is the general supervisor of the groups that provided the scientists and technicians who did the work. J.A. Boa and D.M. Walley provided grouting expertise and made the permeability tests; J.E. Rhoderick and J.P. Burkes were responsible for x-ray diffraction and scanning electron microscopy while A.D. Buck provided consultation and review; J.E. Rhoderick also contributed to planning, intergroup communication, and scheduling; R.E. Richter made the chemical analyses; R.E. Reinhold supervised and took part in physical tests of materials and production of grout specimens; W.G. Miller provided consultation and review on chemical methods and physical testing of materials and grouts.

Col. N.P. Conover, CE. was Commander and Director of WES during the earlier phases of this work; Col. Tilford C. Creel was Commander and Director during the later phases of this work.

20.0 Appendices

A. PSU Experimental Methods
   1. Early Volume Change
   2. Longitudinal Dimensional Change

B. WES Instructions for Joint Program Including
   WES Control Procedures for XRD (Incl 1) and
   WES Control Procedures for SEM (Incl 2)

Appendix A

Experimental Methods

A.1 Early Volume Change Measurement Method(9)

Bulk volume change of cement pastes at atmospheric pressure and room temperature was measured by the following method: The cement-paste is placed in a water tight flexible membrane container, which is put into a closed vessel completely filled with water. Temperature can be controlled by immersing the system in a water bath. The vessel is connected by a tube filled with water to a small beaker which is suspended from a magnetic recording analytical balance. The membrane container conforms to the volume change of the cement sample, so that water from the beaker is sucked into the vessel containing the sample (Fig. A1). The weight change of the beaker due to decrease or increase in amount of water is continuously recorded.

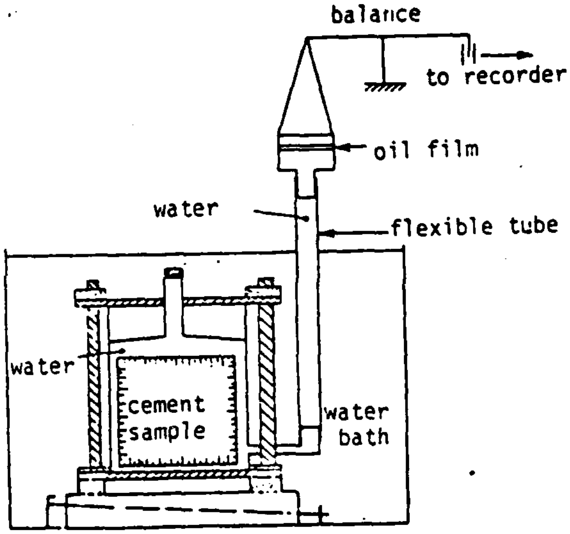

Figure A1.
Instrument for Measuring Volume Change at Atmospheric Pressure

a. From preliminary tests it was found that the optimal sample size is 400 g of paste (the smaller the size, the larger is the scatter in the results). Different kinds of rubber were checked to find a flexible material thick enough to resist irregularities in the surface of the paste due to entrapped air. Preliminary experiments showed that bleeding interferes with the measurement of bulk volume change. This point probably needs an explanation: After mixing cement with water, the cement particles start to settle under gravity leaving free water on the upper surface. This phenomenon is known as "bleeding." In a sealed specimen the water of bleeding will be sucked back since the pores become partly empty as hydration continues. When measuring volume change of a sealed specimen this process of suction of bleeding water will be measured as part of bulk volume reduction while actually it represents part of the inner shrinkage. Bleeding generally reaches its maximum after about 2 hours for water/cement ratio 0.4-0.6 and then suction will reduce gradually the amount of water on the surface. For this reason, bleeding water is generally removed at 2 hours after mixing. The removal is done through the rubber membrane by a syringe and the membrane was sealed after the removal of the water. This method is described in more detail in ref. (9).

A.2 Early Longitudinal Dimensional Change Apparatus (Including Elevated Temperature and Pressure

Early linear dimensional change measurement apparatus, with the option of measuring at elevated temperature and pressure has been designed to measure characteristics of fresh cements/cementitious material under simulated borehole conditions. The apparatus was designed and constructed to permit measurements of early stage behavior at temperatures to 300°F (150°C) and pressures to 3000 psi (21 MPa). It accommodates a one-inch by one-inch (25.4 mm) square cross-sectional sample up to seven inches (178 mm) in length (Fig. A2).

The linear movement of the sample (sealed in the mold) is converted to an electrical signal by the movement of rod/plunger inside an LVDT. The LVDT output is amplified, buffered, and can be displayed on a strip-chart recorder or digitized for use with HP9825A computer.

The sample holder can be placed inside an autoclave or pressure vessel which in turn can be placed in a resistance pot-type furnace, thus providing a controllable pressure-temperature environment over extended periods of time. A block diagram of the complete system is shown separately (Fig. A3). The mixture is placed in the sealed mold, and consolidated to fill. Measurement "zero" starts when the sample is partly consolidated to support the mass of the rod/plunger, and measures both positive and negative displacement.

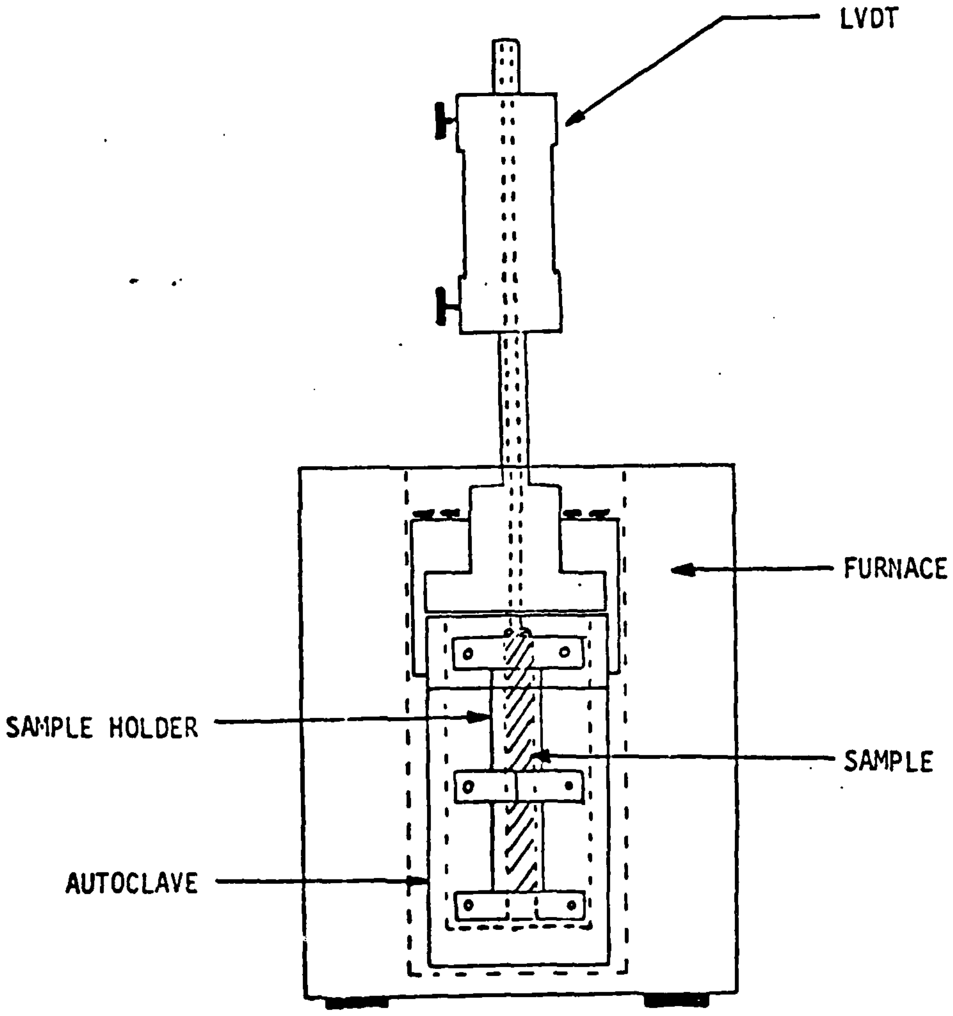

Figure A2. Sample holder for linear dimensional change measurements at a wide range of temperatures and pressures

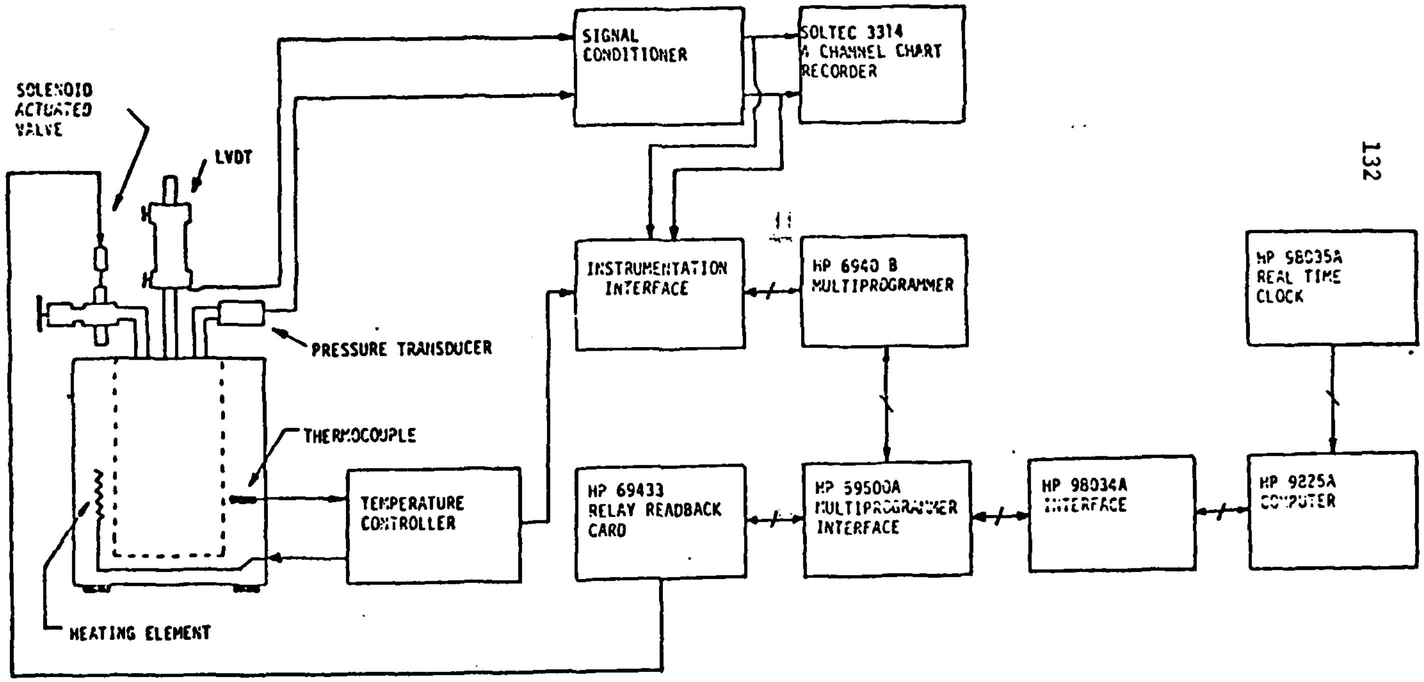

Figure A3. Block diagram of system for measuring linear shrinkage expansion.

Appendix B

DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION, CORPS OF ENGINEERS
P. O. BOX 631
VICKSBURG, MISSISSIPPI 39180

IN REPLY REFER TO:
WESSV

Drafted 27 June 1980
Revised August 1980
Revised 15 September 1980

MEMORANDUM FOR ALL CONCERNED NO. 2096-D JOB NO. 441-S866

SUBJECT: FY 80 Geochemical Program - Structures Laboratory (SL): Milestone No. 3: Joint PSU/WES Experimentation to Develop Precision and Accuracy Data

1. Authority: As in basic memo.

2. Background: Milestone No. 3 of the WES FY 80 program is the development of precision and accuracy data on the methods and procedures used in the evaluation and characterization of the basic materials and grout mixtures.* This effort of WES and The Pennsylvania State University (PSU) will culminate in a joint report to ONWI. The grout mixture that will be used for this study is a variation of BCT-1-FF with mixing water containing $CaSO_4$ and NaCl. the proportions are given in Table 1.

3. Materials:

a. RC-853(2), three bags of Class H cement from the Maryneal plant of Lone Star Industries at Sweetwater, Texas, received 11 June 1980; stored in plastic bags in 30-gal steel drums.

b. AD-592(4), a 55-gal drum of fly ash from the Harrington plant of Southwest Public Service, Amarillo, Texas, received 13 February 1980.

c. AD-626, an expansive admixture, and AD-627, an experimental water reducer, received 13 February 1980. AD-626 is stored in a 55-gal drum.

d. AD-599, a defoamer, received 2 April 1979.

e. AD-640, one hundred and thirty 100-lb bags of Carey's Coarse Granulated Salt, from the Vicksburg Cooperative, Highway 61 Bypass, Vicksburg, Miss., Received in early January 1977.

---

* Paragraph 3.0, Objectives, Program Plan for FY 80, Structures Laboratory, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miss.

The materials listed above are identified by Structures Laboratory serial numbers. PSU will use their supplies of the same items, identified as they see fit.

f. Mixing water, deionized, boiled, and stored in closed containers that are clean, filled, and well stoppered.

4. Tests:

Cement and Pozzolan Group:

(1) Complete chemical and physical tests of RC-853(2), to include Al_2O_3 and Fe_2O_3 by atomic absorption; Mn_2O_3, P_2O_5, TiO_2, SrO, BaO; C 204 and ASTM C 430 (Fineness of Hydraulic Cement by the No. 325 (45-µm) Sieve); 3-, 7-, and 28-day cubes. Make all tests on samples from each of the three bags of cement. Report the results of C 188. (We have C 204, C 188, and 3- and 7-day cubes; 28-day cubes have been cast.)

(2) Additional tests of AD-592(4): Fineness by C 204; Mn_2O_3, TiO_2, P_2O_5, SrO, BaO also, as for the cement.

(3) Mix the grout (Table 1) in a Hobart mixer. After measuring out the needed masses of cement, fly ash, expansive additive, and water-reducing admixture, pre-blend them. Add the measured mixing water and defoamer to the clean bowl. Add the solids to the water and defoamer. Turn on mixer and mix at slow speed with the stainless steel wire whip for 1 min. Stop the mixer; scrape down the insides of the bowl and let the mixture rest for 30 sec total including scrapedown. Start the mixer at slow speed and mix to a total elapsed time of 5 min. Fill the flow cone; remove thumb from opening at the bottom of the flow cone at 6 min. Measure flow time (CRD-C 79-58*). Return material used to determine flow time to mixing bowl and remix 15 sec.

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* U.S. Army Engineer Waterways Experiment Station, CE, Handbook for Concrete and Cement, with quarterly supplements, Vicksburg, Miss., August 1949.

(4) Cast 2- by 2- by 2-in. cubes to provide tests of three cubes each at 3, 7, 28, 56, 90. 180, and 365 days. Store sealed molds at 38°C for 24 hr ± 1/2 hr, then strip. Notify P. Burkes that the above have been stripped, so that he can measure their specific gravity in the Cement and Pozzolan Group. Then cure all specimens at 38°C in a tank of saturated $Ca(OH)_2$. Break the cubes in compression, loading plane-molded surfaces at each age.

(5) Cast 12 vials of grout to be stoppered and held at 38°C in the tank of saturated $Ca(OH)_2$ for examination by Buck. Notify Rhoderick when vials are cast.

(6) Cast six 1- by 1- by 11-1/4-in. bars and hold them sealed at 38°C for 24 hr ± 1/2 hr, then demold. Cure in the same manner as described in paragraph 4b(4). Notify Dan Wilson or Dale Glass when the bars have been stripped and placed in the 38°C tank of saturated $Ca(OH)_2$ solution, so that they can make the 24-hr initial weight and resonant frequency measurements.

(7) Cast bars for restrained expansion. Test according to ASTM C 806, with the exception of using grout rather than the standard mortar. Measure the restraining bar before casting; make the first measurement of the bars at 24 hr. Cure and store the restrained bars in a separate tank of saturated $Ca(OH)_2$ solution at 38°C.

(8) Cast two 6- by 12-in. cylinders and cure in the same manner as described in paragraph 4b(4). Notify Grouting subgroup (Don Walley) when specimens are cast. Cast the cylinders after it is clear whether the new permeability equipment has been tested and shown to be satisfactory or whether we should use the older equipment. In any case, 28- and 7-day permeability must be reported before the end of October 1980.

b. <u>Evaluation and Monitoring Group, Engineering Physics Unit</u>: Remove from the curing tank the three 1- by 1- by 11-1/4-in. bars. Weigh each and determine resonant frequency, then calculate dynamic modulus of elasticity according to ASTM C 215. Return to curing tank, test again at each age of strength test (3, 7, 28, 56, 90, 180, 365 days).

c. <u>Concrete and Grouting Group, Grouting Unit</u>:

(1) Supply Cement and Pozzolan Group with a flow-cone apparatus.

(2) Prepare a curing tank in the 100°F room. The curing water should be saturated with $Ca(OH)_2$.

(3) Remove from curing tank a 6- by 12-in. cylinder and cut to a 6-in. diameter 6-in. long cylinder and test in water permeability at 7 days age using deionized water. Return it to the curing tank and cure to a total of 28 days, then retest. If it is impossible to retest the same cylinder, test the second cylinder at 28 days. If one or both cylinders are in good shape after test, retain for later testing.

Materials and Concrete Analysis Group, Petrography and X-Ray Unit:

(1) P. Burkes will bring the stripped cubes to the Section while the cubes are being stripped and weigh each cube to be tested in air and water after stripping. Calculate bulk specific gravity according to ASTM C 642.

(2) Remove from the curing tank a vial at 3, 7, 28, 56, 90, 180, and 365 days. Prepare each sample by sawing a 2- by 1- by 1/4-in. slab from the center of the vial. Smooth the sawed surface using methanol until saw marks are gone. Keep specimens and slabs in methanol and place in freezer if necessary. X-ray patterns will be made with an X-ray diffractometer using nickel-filtered copper radiation. The sample will be placed inside a vapor hood during X-ray diffraction. The hood will have an environment of static nitrogen and a sponge soaked with saturated barium hydroxide solution. The X-ray diffraction unit will be standardized before use each day (Incl 1) and a fast pattern (2°/min) and a slow pattern (0.2°/min) made.

(3) Examine the grout at 3 and 28 days by scanning electron microscopy. Break the specimen transversely, dry in a vacuum at 60°C* for not more than 15-1/2 hr, break again to get a convenient sized piece to mount on a sample stub, preferably with the fracture approximately parallel to the long axis of the cylinder. Coat the sample with carbon, then with an 80:20 mixture of gold to palladium. National Bureau of Standards Standard Research Material (SRM) 484 (Incl 2) will be used monthly to verify that magnifications are proper. Resolution is checked monthly using Research Material 100 (Incl 3).

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* It has been discovered through experimentation that 60°C will affect the ettringite on the outside surface of a sample. However, since we examine a freshly fractured surface, and not the outside surface, this should not be a problem.

WESSV 15 September 1980

SUBJECT: FY 80 Geochemical Program - Structures Laboratory (SL):
Milestone No. 3: Joint PSU/WES Experimentation to
Develop Precision and Accuracy Data

5. Schedule: The work should begin as soon as possible and be expedited along the way as it needs to be completed this FY. However, if it cannot be completed, a draft report will be prepared in FY 80.

6. Report: Provide all the data to J. Rhoderick. He will tabulate it and write the report. The work plan should be mailed to Dr. Della M. Roy before 10 August 1980. The final report will be completed not later than the end of the first quarter of FY 81.

/BRYANT MATHER
Engineer
Chief, Structures Laboratory

3 Incl
as (same as in
initial memo)

CF w/o incl:
B. Mather
K. Mather
Scanlon
L. Newton(QA Officer)
Hoff
Boa (2)
Saucier
Buck (3)
McDonald
Sullivan (2)
Miller (2)
Husbands (2)
OTP&P
F. Burns (ONWI)
D. Roy (PSU)
P. Licastro (PSU)
M. Grutzeck (PSU)

Table 1

Mixture Data for Grout

Constituents	Mass, g	Mass, %	Mass, g, for 0.1 cu ft†
Cement H (RC-853(2))	68.0	50.84	2960
AD-492(4)	22.9	17.12	997
AD-626	8.3	6.20	361
NaCl	4.05	3.03	176
AD-627	1.10	0.82	48
AD-599	0.02 mℓ*	0.01	0.58
Water (deionized or distilled and boiled)	29.4	21.98	1280
	133.7	100.00	5822.58
(AD-626)**	(2.5)		
	(136.2)		

---

* Assuming specific gravity = 1. Probably wrong but probably not as badly wrong as Mass %.

** Added to saturate mixing water with $CaSO_4 \cdot 0.5\ H_2O$. The 2.5 g is the amount added for 0.1 cu ft; thus it is obviously wrong for a mixture with a mass of 133.7 g, and consequently I have not included it in a revised total or the Mass, %.

† 0.0028 m^2.

NOTE: Water-reducing agent as percent of cementitious solids = 0.82/50.84 + 17.12 + 6.20 = 0.82/74.16 = 1.106%; calculated from mass for 0.1 cu ft, 1.11%.

INCLOSURE 1

Control Procedures for X-Ray Diffraction Equipment
at the U. S. Army Engineer
Waterways Experiment Station (WES)
Structures Laboratory

1. The following paragraphs describe methods used at WES to assure that operation of the X-ray equipment is satisfactory.

2. X-ray Diffraction.

a. A standardization procedure has been written and is in effect. This is a daily check made using an external standard (per aquartz) to permit adjustment of X-ray tube voltage and amperage to achieve a predetermined intensity level. Other settings are then made to verify that this intensity occurs at the proper portion on the X-ray chart. The intent of this procedure is to permit X-ray diffraction patterns made at different times with the same unit to be comparable.

b. Peak resolution is used to verify that the combined effects of X-ray tube alignment and goniometer alignment are satisfactory. One procedure is to examine the resolution into $K\alpha_1$ and $K\alpha_2$ components of an X-ray peak of a metal. This is described on page 18 of Directions 11690E, "SPG X-ray Spectrogoniometer for Diffraction and Emission Techniques (Installation, Operation, Maintenance)" in the General Electric (now Diano) XRD-7 Instruction Manual. Another procedure is the test for resolution of five lines of quartz within one degree at about 68 degrees 2θ, this is described on pages 392-393 of Klug, H. P, and Alexander, L. E., "X-ray Diffraction Procedures", 2nd Edition, 1973. The procedure at WES is to check the $K\alpha_1$-$K\alpha_2$ peak resolution on a monthly basis. If the resolution should decrease significantly, then the cause would be found and corrected. The results of the periodic checks are kept for one year.

c. The proper angular location of a diffraction peak has been checked by the use of the 4.26 Å peak of permaquartz. The general validity of this positioning is checked daily as part of the standardization procedure when the location of this peak is found for the intensity check. However, since peak position may change with the type of sample preparation that is used, an internal standard of powdered quartz is added to a sample when peak position is a major concern.

3. In addition to the above procedures, there is a maintenance contract on this equipment so that other phases of satisfactory operation are checked periodically by the field service engineer.

A. D. Buck

A. D. BUCK
Materials and Concrete
Analysis Group
Structures Laboratory

Steps in Standardization of XRD-7

General: Cu tube with 2 layers nickel, 4° target angle, 1° Beam Slit, 3° Soller, 0.2° Detector Slit, 95 ± 2% Acceptance, E_L - 0.2, ΔE - 0.6, CT voltage 2540 (Aug '77) Scale Log 4000 c/s

1. Use log zero and log gain controls to adjust top and bottom of scale (about 15 c/s with low power and 50 c/s with high power)

2. Tune in on apex of 4.24 peak (≈20.81°2θ) of Permaquartz (or Silica standard #1)

3. Adjust power to get the following c/s values for conditions used:

	Permaquartz	Reserve Piece Silica Standard # 1
High Power go above 50 KVCP only as needed to obtain standard intensity (≈21MA)	3650 ± 80 c/s 99-1/2 ± 2 chart units	3435 ± 80 c/s 98-1/2 ± 2 chart units
Low Power (≈29KVCP, 41 MA) If power is low lower MA and raise KVCP	1760 ± 40 c/s 89-1/2 ± 2 chart units	1620 ± 40 c/s 88-1/2 ± 2 chart units

4. If necessary, adjust top and bottom of scale with log zero and log gain controls to get the proper peak intensity in chart units.

The following steps are done to add scale expansion:

1. Use 6 layers of nickel filter and values should drop to

	Permaquartz	Silica Standard # 1
High Power	795 c/s, 72-1/2 chart units	750 c/s, 71 chart units
Low Power	380 c/s, 64-66 chart units	375 c/s, 67-1/2 chart units

2. Now adjust the scale expansion knob to get the following:

	Permaquartz	Silica Standard # 1
High Power	92-1/2 chart units	91-1/2 chart units
Low Power	87-1/2 chart units	86-1/2 chart units

3. Replace 6 layers of nickel filter with regular nickel filter and unit is ready for use.

   1) Use 20 units of zero offset at angles above 20° 2-θ for cement as of 12 April 1973.

   2) Also use 8 second time constant for 2° - 20° 2-θ and 8 second time constant for 20° 2-θ out.

Standardization of XRD 5/6 5 August 1977

General: Cu tube with 2 layers nickel, 4° target angle, 1° beam Slit, 3° soller, 0.2° detector slit, 95 ± 2% acceptance, $E_L = 0.2$, $\Delta E = 0.6$, Gain = 4, CT voltage 1680, log 4000 c/s

1) Use log zero and log gain controls to adjust top and bottom of scale.

2) Tune in an apex of 4.24 peak (≈20.81° 2θ) of permaquartz (or silica standard # 1).

3) Adjust power to get the following values.

	Permaquartz	Reserve Piece Silica Standard # 1
High Power (≈49KVCP, 20+ MA)	2790 c/s 92 chart units	2690 c/s 91 chart units
Low Power (≈27KVCP, 39 MA) if power is low, raise KVCP and lower MA	1025 c/s 71 chart units	990 c/s 70 chart units

machine is ready for use.

INCLOSURE 2

Control Procedure for the Scanning Electron Microscope (SEM) at the U. S. Army Engineer Waterways Experiment Station (WES) Structures Laboratory

1. Overall operation of the unit and any adjustments that may be required are checked periodically by a field service engineer under a maintenance contract. The contract requires two maintenance visits a year as well as emergency calls.

2. Since magnification can be an important feature of SEM micrographs, the validity of calculated magnifications are checked monthly. This is done by use of National Bureau of Standards Standard Reference Material (SRM) 484. This is a stage micrometer having lines on it with known widths between lines. This item and its use is described in Incl 1.

3. SRM 484's serial number is JY-43-DF.

4. The test micrographs of SRM 484 that are made each month are kept for one year.

A. D. Buck

1 Incl
as

A. D. BUCK
Materials and Concrete
Analysis Group
Structures Laboratory

Department of Commerce
Elliot L. Richardson,
Secretary

National Bureau of Standards
Ernest Ambler, Acting Director

National Bureau of Standards Certificate

Standard Reference Material 484

Scanning Electron Microscope Magnification Standard
(A Stage Micrometer Scale)

David B. Ballard and Fielding Ogburn

This Standard Reference Material is intended for use in calibrating the scanning electron microscope (SEM) magnification scale to an accuracy of 5% or better within the range of 1,000 to 20,000X. Each SRM bears an identification number and has been individually measured.

The certified distance between specific lines opposite the Knoop indentation (see the sketch) and the identification number are given in the table below. *The enclosed SEM photograph shows the area used in the measurement of this specific SRM.*

Identification Number: JY-43-DF

Line Pair	Nominal Distance	Certified Distance	Uncertainty
	µm	µm	µm
0 → 1	1	.959	039
0. → 2	2	1.922	039
2 → 3	3	2.869	039
3 → 4	5	5.173	039
0 → 6	50	50.62	.71

The distances between the lines were *determined from measurements made on photographs taken with an* SEM in which each SRM was compared by substitution with a Master Standard. The Master Standard had previously been calibrated by the NBS Dimensional Technology Section using a polarizing helium-neon laser interferometer. The uncertainty of this calibration, based on 81 independent measurements, is 0.004 µm for distances from 1 to 5 µm and 0.009 µm for distances from 10 to 50 µm.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the *Office of Standard Reference Materials by R. E. Michaelis* and R. K. Kirby.

Washington, D.C. 20234
February 1, 1977

J. Paul Cali, Chief
Office of Standard Reference Materials

Recommended Procedure for Calibration of SEM Magnification Using SRM 484[*]

1. Rigidly mount SRM 484 on SEM stub with electrically conductive cement or clamp onto stage of SEM.
2. Surface of SRM 484 should be normal to electron beam.
3. To minimize the distortions produced by the recording system the specific lines on SRM 484 to be used in the calibration should be chosen so that the distance between them corresponds as closely as possible to the length of the object to be measured with both images positioned in the same area on the cathode ray tube (CRT). A millimeter scale taped onto the edges of the CRT on the x and y directions will assist in the relocation on the respective images.
4. Allow a 30 minute or more warm-up of electronic circuits to achieve operational stability.
5. A vacuum of 10^{-4}mm of Hg or better is necessary to keep the contamination rate on the surface of the SRM as low as possible.
6. SEM resolution should be a minimum of 0.05 μm.
   (Good edge resolution is not a necessary requirement.)
7. Adjust final lens current at a resettable value. Cycle lens circuit OFF-ON 3 times to minimize hysteresis effects.
8. Adjust electron gun voltage (between 5 to 30 kV), saturate filament, and check filament alignment.
9. Adjust lens apertures and stigmator for optimum operation (minimum astigmatism).
10. The working distance can be reproducibly obtained by focusing on the gold lines with Z axis control at highest possible magnification to minimize depth of focus. An alternate method is to use "Y" mode and adjust for maximum signal.
11. Add "Black Level" for contrast if necessary, S/N ratio should be 2:1 minimum.
12. Take photograph under best conditions. Allow Polaroid prints to dry 15 to 20 minutes or more to minimize distortion from paper, emulsion and coating shrinkage.
13. Measure the perpendicular distance between each pair of lines on the photograph with a TEM Diffraction Plate Reader or use an equivalent instrument the precision of which is suitable for this purpose (about 0.1 mm).
14. Repeat measurements 3 times on each photograph to determine the average spacing.
15. $$\text{Magnification} = \frac{\text{Distance between lines as measured on photograph}}{\text{Certified distance between same lines}}$$

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[*] A Procedure for Calibrating the Magnification Scale of An SEM Using SRM 484. (To be published as an NBS Technical Note.)

INCLOSURE 3

National Bureau of Standards
Report of Investigation
Research Material 100
Scanning Electron Microscope Resolution Test Specimen (Al-W)

D. B. Ballard

Research Material 100 SEM Resolution Test Specimen (Al-W), is an alloy of aluminum and tungsten in fine dentritic structure formed on the surface of a bead the diameter of which is approximately 5 mm.(1) RM 100 is especially suitable for use as a resolution and performance test material for the Scanning Electron Microscope (SEM).(2)

Material Characteristics

RM 100 has the following characteristics that satisfy the criteria for a resolution test specimen for the SEM The dendrites have a high secondary electron emission, and thus a high contrast which permits ease of stigmator adjustment. There are no loose particles, it is non-magnetic, vacuum clean, has no adverse reaction (melting) to the electron beam, no surface preparation or coating is required and has long term structural stability. Also it has many areas of a variable structure spacing suitable for both high and low resolution testing and the structure has been observed on extracted replicas in the transmission electron microscope (TEM) A specific photomicrograph is provided with each RM 100 to verify the dendritic structure and its location. The four micrographs shown in this Report of Investigation are typical of RM 100 and are provided for information and orientation purposes.

Recommended Application Method

RM 100 should be mounted on its side with conductive cement to a SEM specimen stub. A short bake in a vacuum oven at 60 °C will quickly set the cement. The specimen then is inserted in the SEM stage and tilted toward the scintillator at an angle of ~30°. Selection of instrument operation parameters is at the discretion of the operator.

A photomicrograph is taken at the desired magnification with the Al-W dendrites oriented so that the elongated structures are perpendicular to the axis of tilt. Resolution is determined by measurement on the photo of a 1 mm dark space between

(over)

two nearly equally intense dendrites by eye with a millimeter scale. The following relationship (with appropriate units) can be used to calculate resolution.

$$\text{Resolution } (\mathring{A}) = \frac{10^7}{\text{Magnification}}$$

Absolute measurement of the dentrite size or spacing cannot be made unless the instrument magnification is known. It is recommended that the measurement be made on an unenhanced photograph because additional electronic or photographic modification could bias the instruments' resolution in the secondary emission mode.

(1) Ballard, D. B., A resolution test sample for the scanning electron microscope, Proc. 30th Annual Meeting Electron Microscopy Society of America and First Pacific Regional Conference, Los Angeles, Calif., Aug. 14-18, 1972, p. 446 Claitor's Book Store, Baton Rouge, LA.

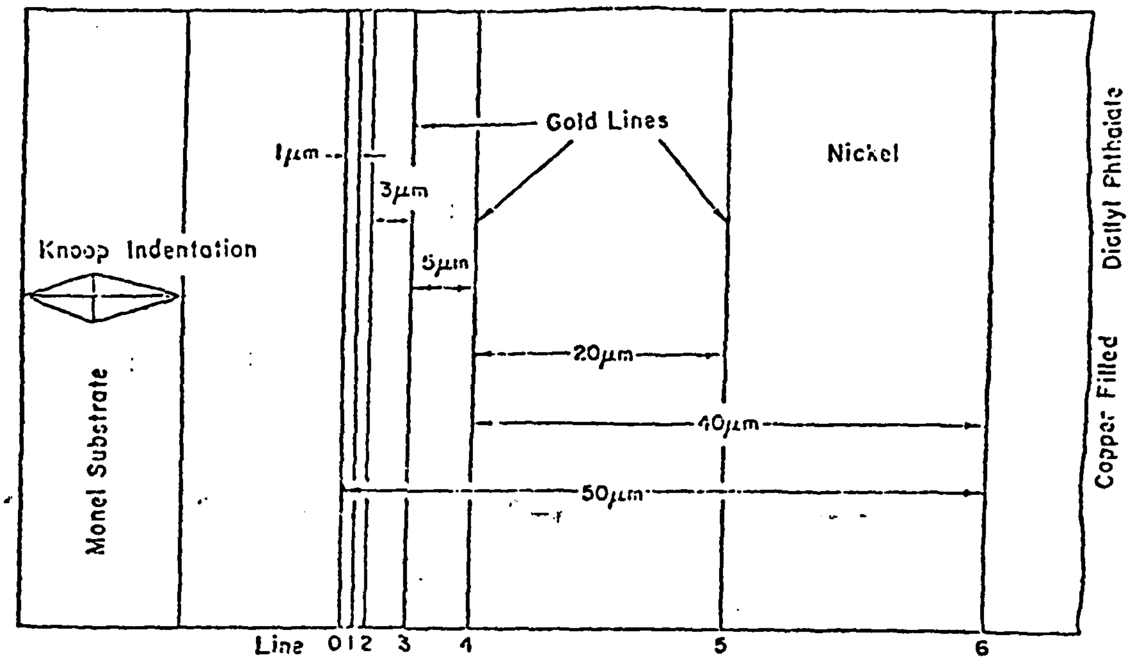
(2) Ballard, D. B., Comparison and evaluation of specimens for resolution standard, Proc. 5th Annual Scanning Electron Microscope Symposium, Part I, IIT Chicago, Ill., Apr. 25-26, 1972, P. 121 (Ed. Dr. Om Johari, Metals Research Division, IIT Research Institute, Chicago, Ill. 60616).

Users of this Research Material are encouraged to report findings and data to:

Research Materials
Office of Standard Reference Materials
Room B311, Chemistry Building
National Bureau of Standards
Washington, D. C. 20234

When a sufficient body of such information has been received, an updated Report of Investigation will be issued by NBS and sent to all purchasers of these materials.

May 11, 1973



The operating conditions of the SEM were monitored and a resolution of 0.050 μm was maintained using an SEM Resolution Test Specimen. (This test specimen, RM 100, is also available from the Office of Standard Reference Materials.) Each reported interval has been corrected for photographic recording system distortion and SEM magnification drift using the Master Standard. The uncertainty values are based on a random selection of samples which were measured 2 to 3 times at intervals that were as long as 3 months.

The polished surface of each SRM has been carefully ground and polished using metallographic techniques. The carbonaceous contamination (a product of SEM electron beam bombardment) can be removed by hand polishing on micro cloth using metallographic grade MgO powder as an abrasive. An alternate cleaning method is to D.C. sputter etch for less than 30 seconds in an argon atmosphere. This cleaning process does not alter the certified spacing of the lines by more than 0.010 μm.

A recommended procedure for calibrating the magnification of the SEM using SRM 484 is given below. It is suggested that the user extend the calibration to adjacent areas outside of the certified area on the standard for routine use as a "Working Standard."

The significant contributions of the following NBS staff members are hereby acknowledged: J. P. Young, for techniques of electroplating; C. H. Brady, for metallographic services; J. S. Beers, for calibration of the Master Standard; J. M. Cameron and M. C. Croarkin, for statistical analysis; and A. W. Ruff, for advice and encouragement.

21.0 GLOSSARY OF PHASES

Alite, C_3S (substituted), Ca_3SiO_5, substituted tricalcium silicate

Belite, C_2S (substituted), Ca_2SiO_4, substituted dicalcium silicate

Calcite, $c\bar{c}$, calcium carbonate, $CaCO_3$

Calcium hydroxide, CH, portlandite, $Ca(OH)_2$

Calcium silicate hydrate, C-S-H

Ettringite, $C_6A\bar{S}_3H_{32}$, 6-calcium aluminate trisulfate-32-hydrate

Quartz, S, silicon dioxide, SiO_2

Tetracalcium aluminate dichloride-10-hydrate, $C_3A(CaCl_2)H_{10}$, Friedel's salt (Chloroaluminate)

Tetracalcium aluminate hemicarbonate-12-hydrate, $C_4A\bar{C}_{0.5}H_{12}$

Tetracalcium aluminate monosulfate-12-hydrate, $C_4A\bar{S}H_{12}$, monosulfoaluminate

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C = CaO
S = SiO_2
A = Al_2O_3
F = Fe_2O_3
$\bar{S}$ = SO_3
$\bar{C}$ = CO_2
H = H_2O

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

PSU/WES Interlaboratory Comparative Methodology Study of an Experimental Cementitious Repository Seal Material : Report 2 : Final results / by Della M. Roy ... [et al]. (Materials Research Laboratory, The Pennsylvania State University and Structures Laboratory, U.S. Army Engineer Waterways Experiment Station). -- Vicksburg, Miss. : The Station ; Springfield, Va. : available from NTIS, 1982.

vii, 149 p. ; ill. ; 27 cm. -- (Miscellaneous paper ; SL-81-2, Report 2)

Cover title.

"March 1982."

"Prepared for Battelle Memorial Institute, Project Management Division and Office of Nuclear Waste Isolation, Battelle Memorial Institute under Subcontract No. E512-04200 and Contract No. DE-A197-81ET46633."

An earlier version of this report was released by the Materials Research Laboratory of The Pennsylvania State University as Report No. ONWI-324. The present title was

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PSU/WES Interlaboratory Comparative Methodology : ... 1982.
(Card 2)

modified slightly by adding the words "Comparative Methodology" and "Report 2 : Final Results" for conformance with the first report in the series.

Bibliography: p. 126.

1. Grout (Mortar). 2. Grouting. 3. Radioactive waste disposal in the ground. 4. Sealing compounds. I. Roy, Della M. II. Battelle Memorial Institute. Project Management Division. III. Battelle Memorial Institute. Office of Nuclear Waste Isolation. IV. U.S. Army Engineer Waterways Experiment Station. Structures Laboratory. V. Series: Miscellaneous paper (U.S. Army Engineer Waterways Experiment Station) ; SL-81-2, Report 2.

TA7.W34m no.SL-81-2, Report 2

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