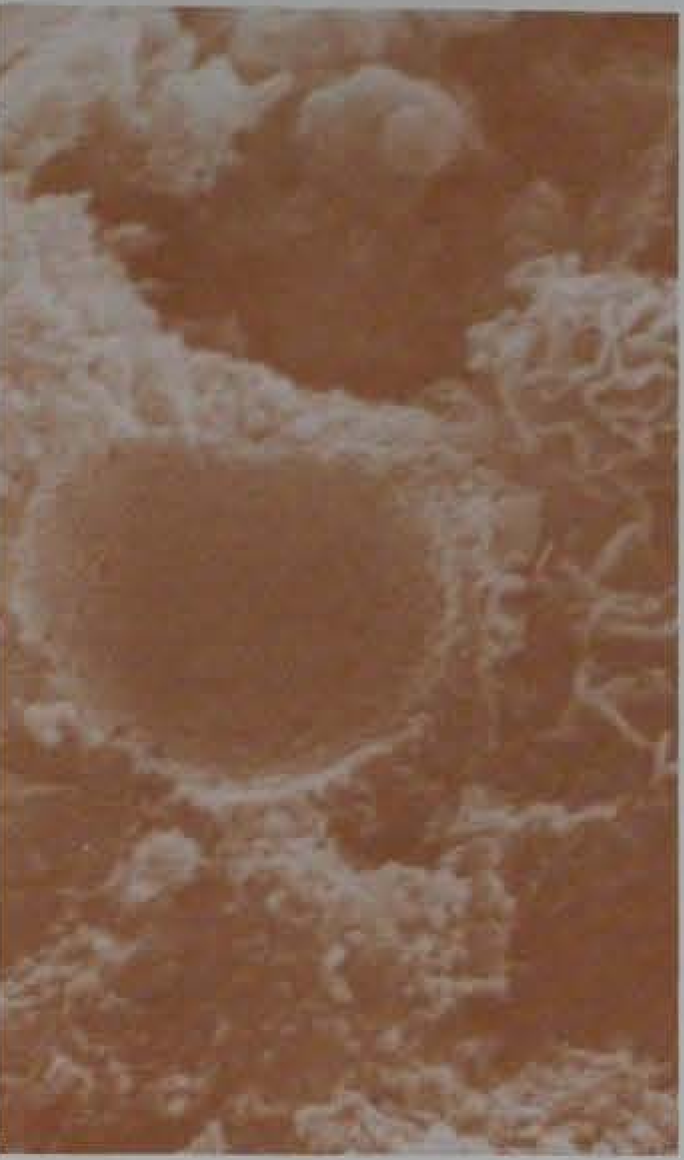
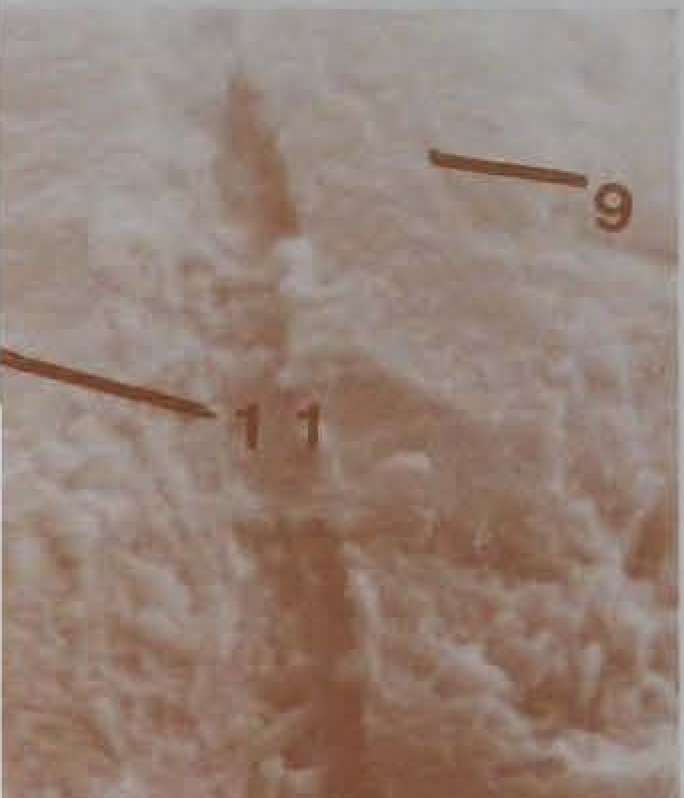
y Corps
eers





STRUCTURES LABORATORY

MISCELLANEOUS PAPER SL-86-2

DEVELOPMENT OF FRESHWATER GROUT SUBSEQUENT TO THE BELL CANYON TESTS (BCT)

by

Lillian D. Wakeley, Donald M. Walley, Alan D. Buck

Structures Laboratory

DEPARTMENT OF THE ARMY
Waterways Experiment Station, Corps of Engineers
PO Box 631, Vicksburg, Mississippi 39180-0631

April 1986
Final Report

Approved For Public Release; Distribution Unlimited

Prepared for

Sandia National Laboratories
Albuquerque, New Mexico 87115

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188
Exp. Date: Jun 30, 1986

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
Miscellaneous Paper SL-86-2

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
USAEWES
Structures Laboratory

6b. OFFICE SYMBOL *(If applicable)*
WESSC

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS *(City, State, and ZIP Code)*
PO Box 631
Vicksburg, MS 39180-0631

7b. ADDRESS *(City, State, and ZIP Code)*

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Sandia National Laboratories

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
Albuquerque, NM 87115

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE *(Include Security Classification)*
Development of Freshwater Grout Subsequent to the Bell Canyon Tests (BCT)

12. PERSONAL AUTHOR(S)
Wakeley, Lillian D., Walley, Donald M., Buck, Alan D.

13a. TYPE OF REPORT
Final report

13b. TIME COVERED
FROM 1979 TO 1985

14. DATE OF REPORT *(Year, Month, Day)*
April 1986

15. PAGE COUNT
56

16. SUPPLEMENTARY NOTATION
Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*
Bell Canyon Test
Grout
Microstructure
Physical properties
Radioactive waste
Repository sealing
WIPP

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

Freshwater grouts are among the cement-based materials developed and studied at the US Army Engineer Waterways Experiment Station (WES) for sealing a radioactive waste repository in bedded evaporite rocks. The grout most studied was first developed for the Bell Canyon Tests (BCT) at the Waste Isolation Pilot Project (WIPP) in southeastern New Mexico.

This salt-free grout, designated BCT-1FF, was placed in the field in 1981 (Site and Preliminary Design Validation, or SPDV) and again in 1983 (B-25 borehole). Casting of specimens for laboratory study at WES accompanied both of these field events. Specimens were tested to ages of nearly four years for such properties as expansion, compressional wave velocity, compressive strength, static and dynamic elastic moduli, and phase composition.

(Continued)

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE *(Include Area Code)*

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. ABSTRACT (Continued).

Most properties achieved the values for which this mixture was developed. Changes in some parameters, such as increases in density and expansion, can be related directly to phase composition and microstructure. The BCT-1FF grout is the baseline candidate freshwater grout for future studies and development of the WIPP as a demonstration geologic repository.

PREFACE

The work described in this report is part of an ongoing research effort accomplished in the Concrete Technology Division (CTD), Structures Laboratory (SL), US Army Engineer Waterways Experiment Station (WES), under contract to Sandia National Laboratories (SNL), Albuquerque, New Mexico. Mr. C. W. Gulick of SNL was Technical Monitor of the field and laboratory studies reported herein, which occurred between 1979 and 1983, with additional laboratory studies through FY 85.

Members of the staff of the CTD Grouting Unit, of which Mr. John Boa, Jr., was Chief, carried out the field activities. Dr. Lillian D. Wakeley and Messrs. Donald M. Walley, Dale Glass, Larry Winters, Tommy Ray, Billy Sullivan, Ronald Reinhold, Alan D. Buck, J. Pete Burkes, and G. Sam Wong contributed to the work. The work was under the supervision of Mr. Kenneth L. Saucier, Chief, Concrete and Evaluation Group, CTD; Mr. John M. Scanlon, Chief, CTD; and Mr. Bryant Mather, Chief, SL. The report was prepared by Dr. Wakeley, with contributions by Messrs. Walley and Buck.

COL Allen F. Grum, USA, was Director of WES. Dr. Robert W. Whalin was Technical Director.

CONTENTS

CONVERSION FACTORS, NON-SI TO SI (METRIC)
UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
Fahrenheit degrees	5/9	Celsius degrees or Kelvins*
feet	0.3048	metres
inches	25.4	millimetres
pounds (force) per square inch	6.894757	kilopascals
pounds (mass) per cubic foot	16.018463	kilograms per cubic metre
pounds (mass) per gallon (US liquid)	80.51963	kilograms per cubic metre

---

* To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: $C = (5/9)(F - 32)$. To obtain Kelvin (K) readings, use: $K = (5/9)(F - 32) + 273.15$.

DEVELOPMENT OF FRESHWATER GROUT SUBSEQUENT TO THE BELL CANYON TESTS (BCT)

INTRODUCTION

1. Research on and development of cement-based materials for the Plugging and Sealing Program (PSP) at the Waste Isolation Pilot Plant (WIPP) site in southeast New Mexico has been underway at the Structures Laboratory (SL), of the U.S. Army Engineer Waterways Experiment Station (WES), since 1975. Early in the Materials Development Program for the WIPP site, placement of specially formulated grouts and concretes was judged to be the principal technique for sealing boreholes and access shafts from the surface to the repository horizon. Since passage of the Nuclear Waste Policy Act of 1982, interest in the WIPP site as a prototype or demonstration site for disposal of high-level radioactive wastes has intensified.

2. Because the disposal horizon at the WIPP site will be excavated in rock salt (composed mainly of the mineral halite), recently developed grouts and concretes -- especially those studied since 1983 -- have been formulated with mixing water that is saturated with NaCl (hereafter called salt-water grout). This is to ensure that the water in the grout does not dissolve the water-soluble host rock, and to provide optimum chemical compatibility between rock and sealing material. However, boreholes and shafts also will penetrate layers of non-halite rocks, including anhydrite ($CaSO_4$), and clastic rocks such as siltstone, above the repository horizon. Plugging and sealing materials for use in these rock layers will not include NaCl, as previous studies have shown poor bonding between salt-containing grouts and anhydrite (Gulick, Boa, and Buck 1980; Wakeley and Roy, 1985).

3. Prior to FY 85, fresh-water grouts were the focus of much of the materials development program at the SL. This report describes two series of field tests at the WIPP site involving fresh-water grouts; and physical and mechanical properties, phase composition, and microstructure of specimens of those grouts cured and studied in the SL, to three-years age. Selected data from earlier tests of related fresh-water grouts are presented for completeness.

BACKGROUND: THE MATERIALS DEVELOPMENT PROGRAM

4. The main purposes of the materials development program at the SL, in support of the repository-sealing program at the WIPP site, are:

a) to develop materials and techniques for plugging boreholes and sealing shafts through and near underground facilities for disposal of high-level wastes;

b) to emplace test plugs that will prevent liquids and gases from moving toward or through the salt beds enclosing the repository;

c) to develop materials that will maintain seal integrity for whatever time is required by the total repository design -- probably hundreds to thousands of years (other components of the total system will have other design lives).

5. Through FY 85, the SL materials development program combined an extensive program of laboratory research on materials and techniques, with field supervision and quality control of grouting operations. This was to ensure transfer of proportioning and placement methods developed in the laboratory to on-site operations at the WIPP site (see Appendix A for more about WES involvement in field-support studies). Laboratory research accompanying the field placements entailed development of new mixtures for repository sealing; and study of field-cast samples, which were either prepared at the time of field tests or recovered by later drilling.

6. Desirable properties for which grouts were developed include: homogeneity, pumpability, and long working time when fresh; low permeability, low porosity, high strength, expansive potential, good bonding to the host rock, and long-term durability when set. To achieve these properties, grouts were formulated with various combinations of coarsely ground cement, high-range water reducers, set retarders, chilled mixing water, calcium sulfate additives, fly ash, and low ratio of water to cementitious solids.

7. Grouts placed underground at the WIPP site during the early 1980's were derived from grouts first developed for the Bell Canyon Test (BCT) series in 1979. Both salt-water and freshwater versions of the BCT grout were proportioned using Class H cement, a calcium-sulfate expansive additive, and Class C (high calcium) fly ash. Laboratory studies of these field-cast specimens were described in several previous reports (Gulick, Boa, and Buck 1980, 1982; Gulick and others 1979, Rhoderick and Buck 1981; Rhoderick, Wong, and Buck 1981).

8. Fresh-water grout like that used for BCT tests was placed at the WIPP site in December 1981, in a series of field tests termed Site and Preliminary Design Validation (SPDV). Another grouting event, in September 1983, involved plugging the B-25 borehole at the WIPP site, with fresh-water grout in that portion of the hole that penetrated rock types other than salt.

9. This report: describes field operations for these two test series, SPDV and B-25 fresh-water grout; and summarizes and relates data from WES laboratory tests of properties, phase composition, and micro-structure of specimens cast in the field to accompany these series. Appendices to this report include a summary of field tests with BCT-1FF fresh-water grout that preceded the SPDV and B-25 plugging events (plugs termed ONE and ONEX or 1 and 2). Some data from laboratory testing of specimens cast in the field at the time of these earlier plug tests appear in tables, for comparison to properties of specimens representing SPDV and B-25.

FIELD OPERATIONS: SITE AND PRELIMINARY DESIGN VALIDATION (SPDV)

10. SPDV field work involved grouting the annular area between a steel pipe and the surrounding rock formations. The steel pipe, 10 feet* (3 m) in diameter, was to serve as a ventilation shaft for a demonstration repository at a depth of approximately >980 ft (300 m). Prior to grouting, the open drilled hole 12 feet (3.7 m) in diameter was filled with natural brine, because drill holes in that region of New Mexico commonly fill with this brine from natural sources. The

---

* A table of factors for converting non-SI units of measurement to SI (metric) units is presented on page 3.

steel pipe was grouted through the lower of the two aquifers in the Rustler Formation (non-evaporite rocks), between 792 to 687 ft (241 and 209 m), depth, with the toe of the pipe at the top of the repository rock unit (Salado Formation). The operation required 5700 ft^3 (161.5 $meters^3$) of grout, which displaced the brine as the annulus was filled. Stormont (1984) summarized WIPP-site stratigraphy.

11. The grout used for SPDV field operations was equivalent to that of the BCT-1FF borehole plugging tests with fresh-water grout in 1979 (Gulick et al. 1980). Components and proportions are listed in Table 1. Additional information about procedures of mixing and placing appears in Appendix B. Data on chemical compositions and properties of grout components are in Appendix C.

Field Tests of Fluid Grout

12. Four hours elapsed from the time the grout was mixed in the field until the annulus around the steel pipe was filled. Flow time, time of set, and unit weight were measured frequently during placement operations. Standard test methods for these properties of the fluid grout are listed in Appendix D. Pumping rates and pressures, and grout temperature also were monitored. Representative data from these measurements appear in Table 2.

Laboratory Testing

13. A variety of specimens was cast during mixing and pumping operations, to be transported to the SL for periodic testing of physical and mechanical properties, and for studies of mineralogy and microstructure. Specimen types and sizes are listed in Table 3. These specimens were either coated with a strippable plastic membrane, or sealed in plastic cylinders with tightly fitting lids. Sealed in plastic bags in their original mold or container, they were then transported to WES and cured at laboratory ambient temperature (73°F or 38°C). Rectangular prisms (bar specimens) cast for measurements of linear expansion were not coated with the plastic membrane. Instead, these were placed in an air-tight box in two groups: 1) in plastic bags, on racks over water (at high humidity); and 2) under water that had been saturated with $Ca(OH)_2$.

Testing hardened SPDV grout specimens

14. Studies of the long-term durability of grouts used in WIPP field tests require extensive laboratory testing of field-cast specimens. Properties of hardened grout specimens, tested at intervals of three days to three years after SPDV field placement, include: dynamic and static moduli of elasticity; compressional wave velocity; compressive strength of unconfined specimens; linear and volumetric expansion of restrained and unrestrained prisms; strength of bonding between grout and steel; permeability; porosity; and grain, dry, and apparent bulk densities. Standard test methods, from the Corps of Engineers Handbook for Concrete and Cement, are listed in Appendix D, which also summarizes special procedures for non-standard tests (such as bond strength). Data from testing the properties listed above appear in a subsequent section for comparison with data from other field-cast specimens, introduced in the following paragraphs.

B-25 BOREHOLE PLUG

Field Operations

15. The exploratory borehole designated B-25 was drilled for stratigraphic studies early in 1979, and plugged in September 1983. It extended 842 ft (255 m) from the surface caliche through the Rustler Formation, and an additional 50 ft (15.2 m) into the bedded salt of the Salado Formation. Following placement of saltwater grout in the lower 391 ft (119 m) of the borehole, and a two-day wait to tag the top of the salt plug, fresh-water grout like BCT-1FF was pumped in place, stopping well above the Rustler contact such that evaporite strata and aquifers were sealed. The upper portion of the wellbore column was then filled with sand, with a short surface plug.

16. Field properties of fluid grout were monitored as described for the SPDV operations. Grout components and proportions appear in Table 1, with additional information given in Appendices B and C. This 400 feet^3 (113 meters^3) of fresh-water grout filled the borehole between 740 and 461 feet (225.6 and 140.5 m) in depth.

Laboratory Specimens from B-25 Plugging

17. Cubes, cylinders, and prisms were cast in the field concomitant with field operations, and transported to the SL for controlled storage and periodic testing (as described for SPDV). Test methods were as listed in Appendix D. Test data appear in the following sections.

PHYSICAL AND MECHANICAL PROPERTIES OF FIELD-CAST GROUT SPECIMENS

Non-destructive Tests

Compressional wave velocity

18. Compressional wave velocity is related to the modulus of elasticity of grout. In this test, waves generated by an ultrasonic transducer pass through a specimen of high-modulus grout at greater velocity than they do through grout of lower modulus. Measurements for a group of samples provide a basis for comparison, and indicate if the grout loses its stiffness with time or variations in curing.

19. Measurements on specimens from both field events at various ages appear in Table 4, with some data from previous tests involving BCT-1FF grout (Gulick, Boa, and Buck 1980). Average values for specimens of all three field events at corresponding ages demonstrate a high level of uniformity, considering that the field events represent a two-year time interval and two different grouting contractors. Values for nine specimens show an increase in wave velocity from 6 months to one year. Although the average velocity decreases at two years, the standard deviation also decreased markedly, indicating that the individual specimens may become more uniform with time. This should help in predicting performance of the grout over longer time periods.

20. Compressional wave velocities appear to be independent of specimen dimensions, especially for specimens greater than six months old. However, some specimens were cast by displacing the fluid from brine-filled molds. These specimens show somewhat lower velocities, indicating some dilution and loss of grout quality may occur if it is placed in a fluid-filled borehole.

21. Values for compressional wave velocities are generally between 13,000 and 15,000 ft/sec (3962.4 to 4572 m/sec) (Table 4). These values indicate a dense, high-strength, hardened grout with a low ratio of water to cementitious solids, as is consistent with requirements for borehole-plugging grouts.

22. Dynamic modulus of elasticity, often interpreted as an indicator of general concrete quality (Neville 1981), was determined for SPDV prisms and cylinders at six months, one and two years age (Table 5). Values indicate relatively constant grout modulus over this period. A comparison to values of BCT specimens from placements of plugs 1 and 2 (ONE and ONEX) suggests diminished grout modulus from dilution for plug 1 specimens poured through brine.

Linear and volumetric stability

23. Linear expansion of SPDV grout was monitored for three different sizes of prism specimens, cured either wet (immersed) or dry (coated and bagged), and both restrained and unrestrained. Arrays of specimens from the BCT-1FF Plug 1 and 2 and B-25 events were equally diverse. This complex matrix of sizes, curing conditions, and restraint complicates tabulation and comparison of data from different field events. The data are presented in Tables 5 through 8.

24. Comparison of data for wet and dry-cured prisms with a 2-in. square cross section and 10 in. lengths (51 by 51 by 254 mm) shows decreases in length of dry specimens by two-months age (Table 6). Apparently, the bars were drying in spite of precautions taken to maintain their original water content. Although these dry-cured specimens may simulate conditions underground in some rock units, they are not appropriate for prediction of the behavior of this freshwater grout where it is used to seal casing through aquifers or other water-bearing, non-salt strata (in fact, most rocks are "water-bearing" to some extent).

25. Data for wet storage of SPDV prisms show the following:

a. after nearly four years, prisms are either stable or still increasing in length;

b. expansion of unrestrained prisms is roughly twice that of restrained specimens. Values are about 0.27 per cent for unrestrained and 0.15 percent for restrained prisms at four-years age.

c. Size of prism has no apparent impact on linear expansion.

26. Figures 1 through 3 show similar values for SPDV and B-25 prisms (wet, unrestrained) to 90-days age. However, these prisms from the B-25 field event exhibited linear expansion slightly greater than that of SPDV grout specimens of the same size and curing conditions (Tables 7 and 8). This difference was even greater for restrained specimens (Table 9). Measured expansion of the B-25 prisms is slightly greater with larger specimen size. As anticipated from the results of SPDV tests, unrestrained B-25 prisms show more than twice the expansion of their restrained counterparts (same size and curing conditions); and for each mixture, specimens cured in brine expanded far more than those at laboratory ambient conditions coated with what had been assumed to be an impermeable plastic membrane. In fact, coated SPDV specimens, stored with no additional liquid, showed net length decrease by 28 days and at all test ages thereafter, up to -0.10 percent for three-inch, unrestrained specimens at four years.

27. Lengths of restrained, wet-cured prisms of SPDV grout were measured most recently in September 1985, at nearly four years age. Some SPDV specimens show no increases in length, or very small decreases, suggesting shrinkage of the grout even when immersed in lime water. However, close inspection of the tips of restraining rods showed that by four years age they had corroded, giving rod lengths less than their "zero" values. Therefore, readings of four-year-old specimens suggest shrinkage of the grout that may not have occurred, or may be less than is indicated. The same may be true of younger restrained prisms. Modifications of the method for determining linear stability of specimens cured in a restrained condition, and in a liquid with high ionic activity, will be necessary if such specimens are to be useful in studies lasting several years.

Permeability

28. SPDV cylinders of 6-in. diameter and length were tested for permeability to water at 200 psi (13.8 MPa), by CRD-C48 (See Appendix D). Data from individual specimens were unavailable at the time this report was prepared. Many such tests were judged to have "failed," as indicated by immediate flow through the specimen at a rate too great to be measured. When flow was measurable, it was commonly in the microdarcy range.

Other Tests and Properties of SPDV and B-25 Grouts

Compressive Strength

29. Compressive strength of some of the unconfined SPDV cylinders was measured at ages of 14 days to eight months. Other specimens were stored for possible future use. Table 10 includes these data, plus those for B-25 specimens at 28 and 90 days age, and for Plugs 1 and 2 to two years. Values are similar for all groups of specimens at 28 days (around 11,100 psi, or 76.5 MPa). At greater ages, however, SPDV specimens yield consistently lower strength values, probably a result of dry curing and storage at laboratory ambient temperature.

30. As was noted for expansion prisms, the strippable coating applied to SPDV specimens did not prevent water loss. Lower strength gain may be attributable to partial dehydration. The cylinders from 1 and 2 (ONE and ONEX) field casting were stored in brine water at 100°F. B-25 specimens had slightly lower strength at 90 days than had samples from the other field events.

Other properties

31. SPDV specimens were tested for static modulus and Poisson's ratio at two months after casting. Data from B-25 entail only cylinders 6 by 12 in. (154 by 307 mm), at 56 and 103 days after casting (Table 11). The B-25 data show slight increases in static moduli from one- to three-months age.

32. Tests of bond of hardened grout to steel involved pouring the grout into a steel pipe, and at the desired age, measuring the force necessary to dislodge the hardened grout column (total area of contact). This measure of bond strength is affected by grout expansion or shrinkage, and would be expected to be higher for more expansive mixtures. At 90 days age, bond strength was measured at 570 psi (3.9 MPa). This value is close to bond strength between a similar grout and steel as measured in tensile strength tests at Penn State (Wakeley and Roy 1984), and far higher than bonding measured between related grouts and anhydrite rock (Gulick, Boa, and Buck 1980; Wakeley and Burkes 1985).

PHASE COMPOSITION OF FRESHWATER GROUTS

Sample Preparation and Laboratory Procedures for X-ray Diffraction

Preliminary study of phase compositions of SPDV mixture components

33. Prior to SPDV field operations, dry components of the proposed grout were analyzed by X-ray diffraction (XRD) at the SL. This was essential background information for later study and interpretation of phase compositions of field-cast specimens, and identification of residual, unhydrated and newly formed, hydrated phases, as well as time-dependent changes in the latter. Phase compositions were as expected for these types of starting materials, and similar to those reported elsewhere (Roy et al, 1982).

Storage and preparation of field-cast specimens

34. Most samples used for XRD and microstructural studies were taken from 2-in. cubes cast in the field, like those used for laboratory tests of compressive strength. After the first 24 hrs of curing, in the molds and covered with plastic, exposed surfaces were coated with a strippable plastic membrane, and secured in plastic bags for transport to WES and continued curing and storage. A slice was sawn from a single demolded cube and ground in methanol for each XRD examination.

X-ray diffraction(XRD)

35. A relatively slow scan rate (0.2° 2 Θ /min) gave optimal resolution of peak locations on diffraction patterns, at low power (35 kv, 21 ma) to 20° 2 Θ , and high power (50 kv, 24 ma) to 65° 2 Θ . A fast scan (2° 2 Θ /min) prior to each slow scan provided a check on major compositional changes during the time required for the high-resolution scans. These procedures were constant for six time intervals, ranging from 11 days to 40 months after field casting.

Phase composition of field-cast specimens from SPDV event

36. XRD patterns at each age were examined for residual (unhydrated) portland cement phases, commonly indicated by a peak at 7.3 Å from aluminoferrite, and decreasing amounts of unhydrated calcium silicates. Ettringite and calcium hydroxide (CH) were recognizable hydration products, their relative amounts indicated by intensities of 9.7 Å ettringite and 4.9 Å CH peaks. Quartz, mullite ($Al_6Si_2O_{13}$), and periclase (MgO) remained from the fly ash.

37. Periclase peaks persisted virtually unchanged in intensity for more than three years, suggesting that the crystalline periclase was embedded in other materials so as to be unavailable for chemical reaction until the other materials had reacted. Amounts of unhydrated portland cement phases decreased with time, while ettringite and CH remained fairly constant in this relatively dry condition of storage.

XRD of specimens from other events

38. Phase compositions of samples from the first field placements of this freshwater grout (BCT-1FF Plugs ONE and ONEX) were monitored by XRD through three-years age, and reported by Burkes and Rhoderick (1983). These specimens initially were subjected to elevated temperature (120 and 160°F), and then stored in WIPP-site brine at 100°F. The phase composition of SPDV specimens was compared to that of these older specimens, to determine the effects of temperature and hydration in brine (SPDV specimens having been coated, and cured and stored at laboratory ambient conditions). Phase compositions of the SPDV grout and of other comparable mixtures that have been monitored by XRD are summarized in Table 13.

Discussion

39. Actual differences in phase composition between the SPDV and other specimens are less than might be expected, given the variety of curing conditions. Those specimens stored under water hydrated to a greater extent for a given time

period, as detected by a decrease in peak intensities for UPC. Because the calcium silicate hydrates (CSH) are poorly crystalline, and do not resolve into sharp peaks on diffraction patterns, an increase in CSH with time is difficult to detect. CH does not increase markedly with time, but instead contributes to the total CSH by reacting with silica in fly ash. Therefore, the most reliable indicator of differences in amount of hydration products is comparison of intensities of ettringite peaks.

40. Specimens stored in unfavorable conditions for hydration, especially the SPDV prisms which lost moisture due to insufficient protection, showed essentially no change in amount of ettringite after the first week or so. Most of the specimens of freshwater grouts described in previous reports either had unfavorable storage environments for continued formation of ettringite, or were not monitored for phase changes, or both. However, other work has shown that ettringite can continue to form for at least one year (Buck, Burkes, and Poole 1983).

41. The presence of hydrogarnet in the ONE and ONEX grouts probably is attributable to storage in brine, as is the presence of chloroaluminate. Over relatively short time periods, neither of these phases is expected to have a significant effect on the properties of grout or concrete. However, they exemplify the likelihood of reaction between hydrated cement phases and salts, which could affect long-term durability of seals.

42. Burkes and Rhoderick (1983) described cracking of BCT-1FF specimens immersed in brine. They speculated that this was a response of a grout mixture with high cement content to changes in temperature, moisture, or both. Cubes of the SPDV grout were inspected for cracks before being cut for XRD. None of these dry-stored cubes had been subjected to temperature changes, or cured in brine, and none was cracked, which suggests that the earlier specimens were indeed affected by these environmental conditions. The possibility of this material, when exposed to brines or other groundwater, expanding to the point of losing integrity, suggests potential problems with using expansive grout to seal aquifers at the WIPP site.

43. The fact that amount of ettringite did not increase in dry-cured SPDV specimens is consistent with measured expansion of prisms that were coated and stored at laboratory conditions. All dry-cured SPDV specimens for which length change was monitored showed shrinkage by 28 days, and remained at a fairly constant length (less than their original length) through four-years age. Those that were immersed in brine maintained a fairly constant or slowly increasing length through four years (measured at an age of 3 yrs and 10 mos). Specimens therefore exhibit stability of both length and amount of ettringite.

MICROSTRUCTURE OF GROUT SPECIMENS

Sample Preparation and Laboratory Procedures for Microstructure Studies

44. The procedure for preparing sample surfaces for XRD was described previously. Samples to be studied by scanning electron microscopy (SEM) were cut normal to the XRD prisms, and vacuum dried (45 - 50°C) to remove evaporable water. Each of these smaller prisms was then fractured near one end, to expose a fresh surface, which represented the same phases that were identified by XRD. Coatings of carbon and gold, deposited on the surface to be observed in a vacuum evaporator, kept specimens from charging during SEM observations.

45. Examinations of SPDV specimens at over three-years age gave an opportunity to combine energy-dispersive X-ray analysis (EDX) with SEM. The EDX technique permits elemental analysis of features observed during SEM studies, for elements larger than an atomic number of nine. This provides corroboration of the identity of phases accomplished by recognition of morphologies at high magnification. XRD is useful for identifying well-crystallized phases, and EXD for defining total chemical composition regardless of crystallinity.

Discussion of SEM Observations

46. Several previous reports have included descriptions of SEM examination of grouts or sanded grouts closely related to the SPDV mixture (Burkes and Rhoderick 1983; Buck et al 1983; Roy et al 1982). These reports presented over 50 SEM images, showing microstructure at magnifications of 200 to 20,000 (20K); most show 1K to 5K magnification. Although these images represent several modifications to the mixture, and a suite of curing conditions and ages, they illustrate some microstructural features common and appropriate to most specimens.

47. The matrix of these specimens consists of CSH and CH, interspersed with grains of unhydrated portland cement (UPC), fly ash spheres, and voids. While ettringite is known from XRD to be a major constituent of wet-cured specimens, by SEM it is usually recognized as an apparently minor constituent recognized as elongated hexagonal crystals in void spaces. This disparity suggests that it also is present as crystals too small to be identified by morphology alone.

48. The general change in microstructure that occurs with increasing age, if there is opportunity for hydration to continue, is a densification process, where UPC hydrates and its hydration products (CSH, CH, and ettringite) fill spaces originally occupied by mixing water. While the earliest CSH usually has acicular morphology (Type 1) (Diamond 1976), other forms appear at later ages (Diamond 1976; Jennings, Dalgleish, and Pratt 1981).

49. Magnifications of 5K to 20K reveals details of morphology for specific items, such as form of CSH or small ettringite crystals. The resulting SEM images, however, tend to show just one or a few particles, without any perspective of overall microstructure. Magnification of 200 to 500 shows typical microstructure, but lacks resolution of specific particle types. The SEM images included in this report (Figures 4 through 9) show SPDV specimens at magnifications of 200, 500, 2K, and 10K.

50. Figure 5 is a micrograph in which material having the morphology of CH is present. Silicon also was detected by EDX, indicating that the CH contains CSH (Diamond, 1972). Areas identified by the numbers 8 through 11 on Figure 7 also were studied by EDX. Area 8 is recognizable as UPC, and confirmed as alite or belite by the presence of abundant calcium, less silicon, and a trace of magnesium in its chemical spectrum. The magnesium probably is incorporated in the silicate lattice. The spectrum for area 9 also is dominated by calcium, with less silicon, and smaller amounts of aluminum, potassium, iron, and sulfur. The last four elements are commonly incorporated into the weakly organized crystal structure of CSH, and in this case, may have been derived from the adjacent fly ash sphere.

51. Areas 10 and 11 are the wall of a broken particle of fly ash. The spectra from these regions are similar, dominated by silicon, with less aluminum and calcium, and minor sodium, potassium, and iron. This is a reasonable suite of elements for fly ash glass. The lower image of Figure 9 is an enlargement of Figure 4, again showing the appearance of CSH and fly ash from EDX areas 9 and 11, respectively. These studies reveal the slow reactivity of fly ash, and gradual increase in density with time that was anticipated for the SPDV grout.

DISCUSSION

52. This report includes physical test data on both fluid and hardened grout from the Site and Preliminary Design Validation (SPDV) field event at the Waste Isolation Pilot Plant (WIPP) site in southeastern New Mexico. These data represent nearly four years of sample monitoring. Data from similar specimens from plugging of the B-25 test hole, also at the WIPP site, are included for comparison, as are limited data from the first two field uses of the BCT-1FF freshwater grout (called plugs ONE and ONEX, or 1 and 2). Characterization of SPDV samples includes summaries of phase composition by XRD and observations of microstructure and chemical composition by SEM and EDX, and comparisons to other similar mixtures for which such data have been reported.

53. Predicting Longevity: The potential longevity of the freshwater grout used for these field tests is critical to the repository-sealing effort. Decisions about materials for repository sealing must be made within this century. Therefore, long-term, direct observation of candidate mixtures cannot extend for even tens of years. There is not that much time. The following paragraphs summarize three approaches to studying longevity within this time constraint.

54. Periodic monitoring of laboratory-designed mixtures: Candidate grout mixtures proportioned from laboratory investigations have the advantage of being of known and carefully monitored composition. They give maximum interpretable information when specimens cast in the field or laboratory are cured and aged in controlled environments, and subjected to periodic monitoring of selected properties. The SPDV study represents one such mixture, which was originated in the laboratory and placed in the field. Better definitions of environmental parameters to be simulated during storage, and ranking and quantification of desired mixture properties, would increase the usefulness of data derived from such studies.

55. Old and Ancient Cements: The opposite of short-term monitoring is testing and analysis of specimens of cementitious mixtures that have retained their integrity for hundreds or thousands of years. Mixture formulations and environmental parameters seldom are known well enough for these materials to permit interpretation of causal relationships, as is possible for laboratory-derived mixtures. One can reasonably expect to exceed the properties of these materials by careful selection and proportioning of materials. However, old and ancient mortars and concretes at least define a minimal expectation for longevity. Roy and Langton (1982, 1983) reported data from examinations of cementitious materials of up to 7500 years old. Their 1983 studies indicate the complexity of applying modern methods of chemical analysis, in what amounts to detective work on the nature of original mixture components.

56. Geochemical Modelling: The third approach is one of prediction based on geochemical data. It involves: studying all available data about a given mixture and its components; postulating and quantifying environmental conditions; predicting probable long-term reaction products under these conditions; and predicting longevity from thermodynamic calculations derived from all of these.

57. Each of these three methods provides a portion of the total knowledge base required for ensuring the level of repository safety demanded by the public. This report contributes to the first approach. Recent work at The Pennsylvania State University (Roy and Langton 1982, 1983) began the second. Future research at the Structures Lab will involve the third.

CONCLUSIONS AND RECOMMENDATIONS

58. Physical properties, phase compositions, and microstructure of the SPDV grout at up to four-years age achieved many of the values and characteristics for which this mixture was developed. Changes in some parameters, such as increases in density and expansion, can be related directly to phase compositions and microstructure. These various methods of analysis should be interrelated in future studies, to optimize the usefulness of available information.

59. Long-term studies such as this establish baseline data on performance of grout not exposed to aggressive agents from which the impacts of aggressive agents on specimens of grout or concrete can be determined. Given the working assumption that at some time the repository seals will be breached, consideration of factors that would lead to seal failure is essential. Potential agents that could lead to seal failure involve loading, chemical attack, or environmental influences. Loading is dependent on geologic conditions, and can be simulated in the laboratory in static or dynamic; cyclic or monotonic;, uniaxial or triaxial; compressive, tensile, torsional shear, or dynamic modes. Chemical attack may stem from within, especially in mixtures containing unstable constituents; or from external agresssive influences, such as acid attack or sulfate attack. Environmental deterioration might result from thermal stresses, wetting and drying, changes in groundwater supply and movement, or combinations of these.

60. Calcium silicate hydrate (CSH) is the most important constituent of mixtures based on hydraulic cement. The lack of fixed crystalline structure, variety of morphologies, and range of chemical compositions of CSH preclude simple causal relationships in questions of stability and longevity. Energy-dispersive X-ray (EDX) techniques, in conjunction with SEM observations, provide a tool for studies of structure-property relations. An integrated approach from the outset, such as that attempted after-the-fact for the SPDV studies, will be essential for any future research on cement-based materials for disposal of radioactive wastes.

REFERENCES

Buck, A. D., Burkes, J. P., and Poole, T. S. 1983. "Thermal Stability of Certain Hydrated Phases in Systems Made Using Portland Cement," Miscellaneous Paper SL-85-7, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Buck, A. D., and others. 1983. "Modification of Bell Canyon Test (BCT) 1-FF Grout," Miscellaneous Paper SL-83-18, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Burkes, J. P., and Rhoderick, J. E. 1983. "Petrographic Examination of Bell Canyon Tests (BCT) 1-FF Grouts over a Three-year Period," Miscellaneous Paper SL-83-12, US Army Engineer Waterways Experiment Station, Vicksburg, MS (also SAND83-7115).

Diamond, S. 1976. "Cement Paste Microstructure - An Overview at Several Levels," in Hydraulic Cement Pastes: Their Structure and Properties, Proceedings of a conference held by the Cement and Concrete Association of Great Britain at Tapton Hall, University of Sheffield, 8-9 April 1976.

_________. 1972. "Identification of Hydrated Cement Constituents Using a Scanning Electron Microscope - Energy Dispersive X-ray Spectrometer Combination," Cement and Concrete Research, Vol 2, No. 5. pp 617-632.

Gulick, C. W., Jr., Boa, J. A., Jr., and Buck, A. D. 1982. "Borehole Plugging Materials Development Program," Report 3, SAND81-0065, Sandia National Laboratories, Albuquerque, NM.

_________. 1980. "Bell Canyon Test (BCT) Cement Grout Development Report," SAND80-1928, Sandia National Laboratories, Albuquerque, NM.

Gulick, C. W., Jr., and others. 1979. "Borehole Plugging Materials Development Program," Report 2, SAND79-1514, Sandia National Laboratories, Albuquerque, NM.

Jennings, H. M., Dalgleish, B. J., and Pratt, P. L. 1981. "Morphological Development of Hydrating Tricalcium Silicate As Examined by Electron Microscopy Techniques," American Ceramic Society Journal, Vol 64, No. 10, pp 567-572.

Rhoderick, J. E., and Buck, A. D. 1981. "Examinations of Simulated Borehole Specimens," Miscellaneous Paper SL-81-7, US Army Engineer Waterways Experiment Station, Vicksburg, MS (also SAND81-7109, ONWI-247).

Rhoderick, J. E., Wong, G. S., and Buck, A. D. 1981. "Examination of Samples of Bell Canyon Test 1-FF Grout," Miscellaneous Paper SL-81-5, US Army Engineer Waterways Experiment Station, Vicksburg, MS (also SAND81-7110, ONWI-246).

Roy, D. M., and Langton, C. A. 1983. "Characterization of Cement-based Ancient Building Materials in Support of Repository Seal Materials Studies," ONWI-523, Office of Nuclear Waste Isolation, Columbus, OH.

Roy, D. M., and Langton, C. A. 1982. "Longevity of Borehole and Shaft Sealing Materials: 2. Characterization of Cement-Based Ancient Building Materials," ONWI-202, Office of Nuclear Waste Isolation, Columbus, OH.

Roy, D. M., and others. 1982. "PSU/WES Interlaboratory Comparative Methodology Study of an Experimental Cementitious Repository Seal Material," Miscellaneous Paper SL-81-2, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

Stormont, J. C. 1984. "Plugging and Sealing Program for the Waste Isolation Pilot Plant (WIPP)", SAND84-1057, Sandia National Laboratories, Albuquerque, NM.

Wakeley, L. D., and Roy, D. M. 1985. "Cementitious Mixtures for Sealing Evaporite and Clastic Rocks in a Radioactive-waste Repository," Miscellaneous Paper SL-85-16, US Army Engineer Waterways Experiment Station, Vicksburg, MS.

TABLE 1. Components and Proportions of Fresh-water Grouts Used in Field Tests at the Waste Isolation Pilot Plant (WIPP) Site

	Mass Used Per Cubic Foot of Grout Made, lb.			
Grout	BCT-1FF(1)	BCT-1FF(2)	SPDV	B-25
Component:				
Class H cement	69.82	69.68	73.73	70.31
Fly ash	23.76	23.71	24.65	23.79
Ca(SO)4	8.50	8.48	4.93	8.99
Dispersant	0.925	1.12	0.73	1.06
Defoamer	0.02	0.02	0.02	0.20
Water	28.33	27.81	27.89	25.78
TOTAL	131.36	130.82	131.95	129.13

	Density, Mg/m^3			
fly ash	2.84	2.63	2.24	2.17
cement	3.21	3.23	3.19	3.17

TABLE 2. Properties of Fluid SPDV Grout Measured in the Field

Grout	BCT-1FF (1)	BCT-1FF (2)	SPDV	B-25
Fluid density: lbs/gal	17.6	17.5	17.6	17.4
Ratio of water to cementitious solids, by mass	0.28	0.27	0.27	0.25

TABLE 3. Specimens of SPDV Grout Cast in the Field for Laboratory Tests

Number	Type
9	cylinders cast in metal molds, 6X12 in
21	cylinders cast in pastic molds, 6X12 in
39	cylinders cast in metal molds, 3X6 in
33	2-in cubes
7	cylinders cast in plastic molds, 3X13 in
3	grouting cast in lengths of steel pipe, 3 in X 10 ft

All specimens were capped or coated 3 times with a quick-drying plastic membrane soon after casting and stored at WES in sealed plastic bags at laboratory ambient conditions.

TABLE 4. Compressional Wave Velocity for SPDV and B-25 Specimens.

A. SPDV[a]		6 months	1 year	2 years
2X12-in cores[b]	$\bar{x}$	13075 ft/sec	13514 ft/sec	12978 ft/sec
	s.d.[c]	145.6	201.0	47.9
	no.[d]	9	9	9
6X12-in cylinders	$\bar{x}$		13060 ft/sec	13052 ft/sec
	s.d.			478.0
	no.		2	3

B. B-25[e]		28 DAYS
3X6-in. cylinders	$\bar{x}$	11423 ft/sec
	no.	2

(a) Density = 128.3 lb/ft^3.

(b) Cores drilled from larger specimens.

(c) standard deviation

(d) Number of specimens tested.

(e) Density = 129.6 lb/ft^3

$\bar{x}$

TABLE 5. Dynamic modulus of SPDV specimens

		MODULUS, psi x 10^{-6}		
		6 months	1 year	2 years
A. cured immersed				
1-in. prisms	$\bar{x}$	4.214	4.080	4.092
	s.d.	0.437	0.316	0.404
	no.	7	7	7
2-in. prisms	$\bar{x}$	4.348	4.403	4.439
	s.d.	0.348	0.333	0.326
	no.	4	4	4
3-in. prisms	$\bar{x}$	-	4.108	4.033
	s.d.	-	0.163	0.362
	no.	-	3	3
2X12-in cores	$\bar{x}$	4.942	4.959	4.918
	s.d.	0.073	0.139	0.151
	no.	9	9	9
B. cured dry				
2-in. prisms	$\bar{x}$	3.488	3.634	3.679
	s.d.	0.203	0.244	0.265
	no.	4	4	4
3-in prisms	$\bar{x}$	-	3.599	3.579
	s.d.	-	0.285	0.292
	no.	-	3	3

TABLE 6. Length Change of SPDV Prisms[a] with 2-inch Cross Section (average of 3 bars unless marked).

	LENGTH CHANGE, %			
	STORAGE CONDITION			
	Immersed (wet)		Coated (dry)	
Age	Restrained	Unrestrained	Restrained[b]	Unrestrained
2 days	0.02	0.05	0.02	0.05
7 days	0.05	0.10	0.02	0.05
14 days	0.06	0.13	0.02	0.04
28 days	0.08	0.17	0.01	0.03
56 days	0.11	0.20	-0.02	0.00
180 days	0.12	0.22	-0.03	-0.02
1 year	0.13	0.24	-0.01	-0.03
2 years	0.14	0.25	-0.05	-0.08
3 years	0.15	0.27	not read	-0.04
4 years	0.13	0.27	-0.04	-0.05

[a] Cast 6 and 7 December 1981 at the WIPP.
[b] Average of 2 bars.

TABLE 7. Length Change of BCT 1 and 2 (ONE and ONEX), and B-25 Freshwater-Grout Prisms, Cured Unrestrained and Immersed (wet).

AGE	1 INCH			2 INCH			3 INCH		
	LENGTH CHANGE, %								
	ONE	ONEX	B-25	ONE	ONEX	B-25	ONE	ONEX	B-25
7 days	0.026	0.372	0.114	0.005	0.435	0.120	0.004	0.386	0.126
28 days	0.063	0.455	0.177	0.014	0.457	0.183	-0.006	0.383	0.190
56 days	0.086	0.506	n.r.	0.018	0.484	n.r.	-0.001	0.396	n.r.
90 days	0.098	0.530	0.229	0.018	0.496	0.239	0.001	0.410	0.249
1 year	0.243	0.577	n.r.	0.079	0.573	n.r.	0.007	0.428	n.r.
2 years	0.334	0.584	n.r.	0.158	0.613	n.r.	-0.056	0.452	n.r.
4 years	0.511	1.139	n.r.	0.253	1.058	n.r.	broken	0.890	n.r.

n.r. represents prism lengths not read.

TABLE 8. Length Change of Unrestrained SPDV Prisms of Several Sizes, Stored Immersed (wet), (%).

	LENGTH CHANGE, %		
	Sample size		
Age	1-inch[a] Unrestrained	2-inch[b] Unrestrained	3-inch[c] Unrestrained
2 days	0.05	0.05	0.05
7 days	0.10	0.10	0.10
14 days	0.13	0.13	0.13
28 days	0.16	0.17	0.16
56 days	0.20	0.20	0.23
180 days	0.24	0.22	0.24
1 year	0.26	0.24	0.26
2 years	0.27	0.25	0.27
3 years	not read	0.27	0.29
4 years[d]	0.33	0.27	0.29

[a] Average for 6 prisms.
[b] Average for 3 prisms.
[c] Average for 3 prisms.
[d] Four-year readings taken at 3 years 10 months.

TABLE 9. Length Change of SPDV and B-25 Prisms, Restrained, Stored Immersed (wet)

	LENGTH CHANGE, %			
	2 inch		3 inch	
Age	SPDV	B-25	SPDV	B-25
7 days	0.05	0.06	0.06	0.08
28 days	0.08	0.10	0.11	0.13
56 days	0.10	n.r.	0.13	n.r.
90 days	0.11	0.13	0.14	0.17
1 year	0.12	n.r.	0.16	n.r.
2 year	0.13	n.r.	0.16	n.r.
4 year	0.17	n.r.	0.17	n.r.

n.r. not read

TABLE 10. Unconfined compressive strength of BCT-1FF-type grouts, including SPDV

	COMPRESSIVE STRENGTH, psi (MPa)			
AGE	BCT ONE	BCT ONEX	SPDV	B-25
14 days	10870 (75)	10670 (74)	6685 (46)	- -
28 days	- -	11445 (79)	- -	10810 (75)
56 days	13440 (93)	13850 (96)	11640 (80)	- -
90 days	12750 (88)	15900 (110)	- -	11533 (80)
6 months	13950 (96)	17250 (119)	- -	- -
8 months	- -	- -	12800 (88)	- -
15 months	20750 (143)	22640 (156)	- -	- -

TABLE 11. Static Modulus and Poisson's Ratio for SPDV and B-25 Specimens at Various Ages.

STATUS MODULUS, psi x 10^{-6}

AGE, DAYS	Static Modulus[a] SPDV	Static Modulus[a] B-25	Poisson's Ratio SPDV	Poisson's Ratio B-25
56	-	2.78	-	0.270
61	3.35	-	-	-
103	-	2.87	-	0.290

---

[a] Average of 2 specimens

TABLE 12. Other Properties of Cylinders[a] of B-25 Fresh-water Grout at >60 Days Age

Density, as received (Mg/m^3)	2.08
Oven-dry density (Mg/m^3)	1.86
Grain density (Mg/m^3)	2.80
Porosity (%)	33.41
Moisture Content (%)	11.61
Saturation (%)	64.84
Saturated bulk density (Mg/m^3)	2.20

---

[a] Average of three tests

TABLE 13. Phase compositions of SPDV and other BCT-1FF-type grouts, as determined by X-ray diffraction.

Phases	LABORATORY-CAST GROUT (a)	(b)	(c)	FIELD-CAST GROUT SPDV(d)	(e)
UPC(f)	X	X	X	X	X
$CaSO_4 \cdot 2H_2O$	X(1 day)	X(3 days)	-	-	-
Quartz	X	X	X	X	X
Hydrated phases:					
Ettringite	X	X	X	X	X
Chloroaluminate	-	X	-	-	X
$Ca(OH)_2$	X	X	X	X	X
Hydrogarnet	-	-	-	-	X
Other:					
Salt	-	?	-	-	-

(a) Reported in WES MP SL-81-5, through 90 days, for samples essentially sealed and exposed to up to 150°F and 1500 psi.

(b) Reported in WES MP SL-81-2, through 1 year, for samples stored in lime water at 100°F.

(c) Reported in WES MP SL-83-18, through 1 year, for samples at 100°F for 24h, then in lime water at 73°F.

(d) SPDV, this report, through 3+ years, sealed and stored at 73°F.

(e) Reported in WES MP SL-83-12, through 3 years, stored 100°F.

(f) Unhydrated portland cement phases.

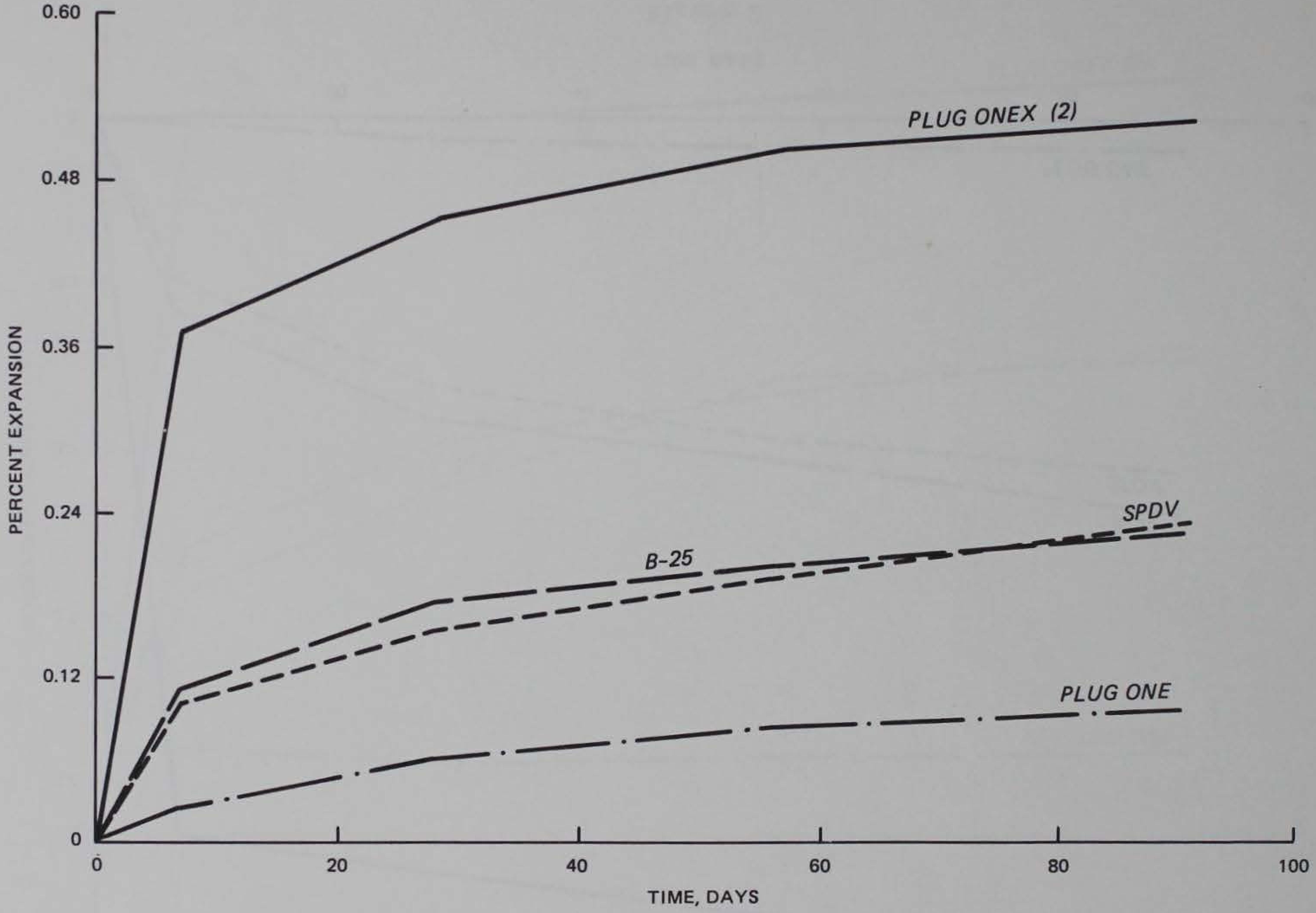

0.60
0.48
0.36
0.24
0.12
0
PERCENT EXPANSION
0
20
40
60
80
100
TIME, DAYS
PLUG ONEX (2)
SPDV
B-25
PLUG ONE

Figure 1

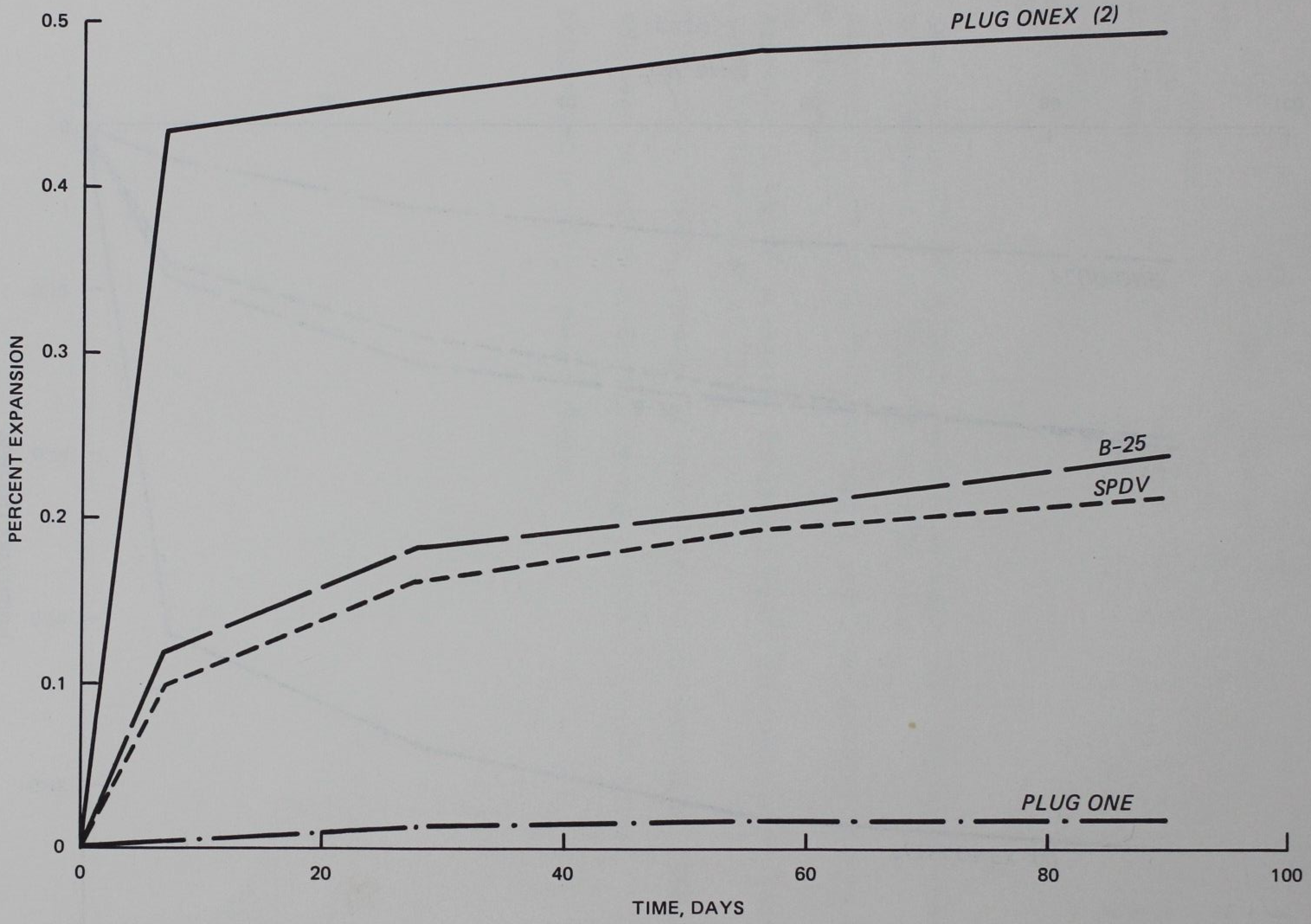

PLUG ONEX (2)
B-25
SPDV
PLUG ONE
PERCENT EXPANSION
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
TIME, DAYS

Figure 2

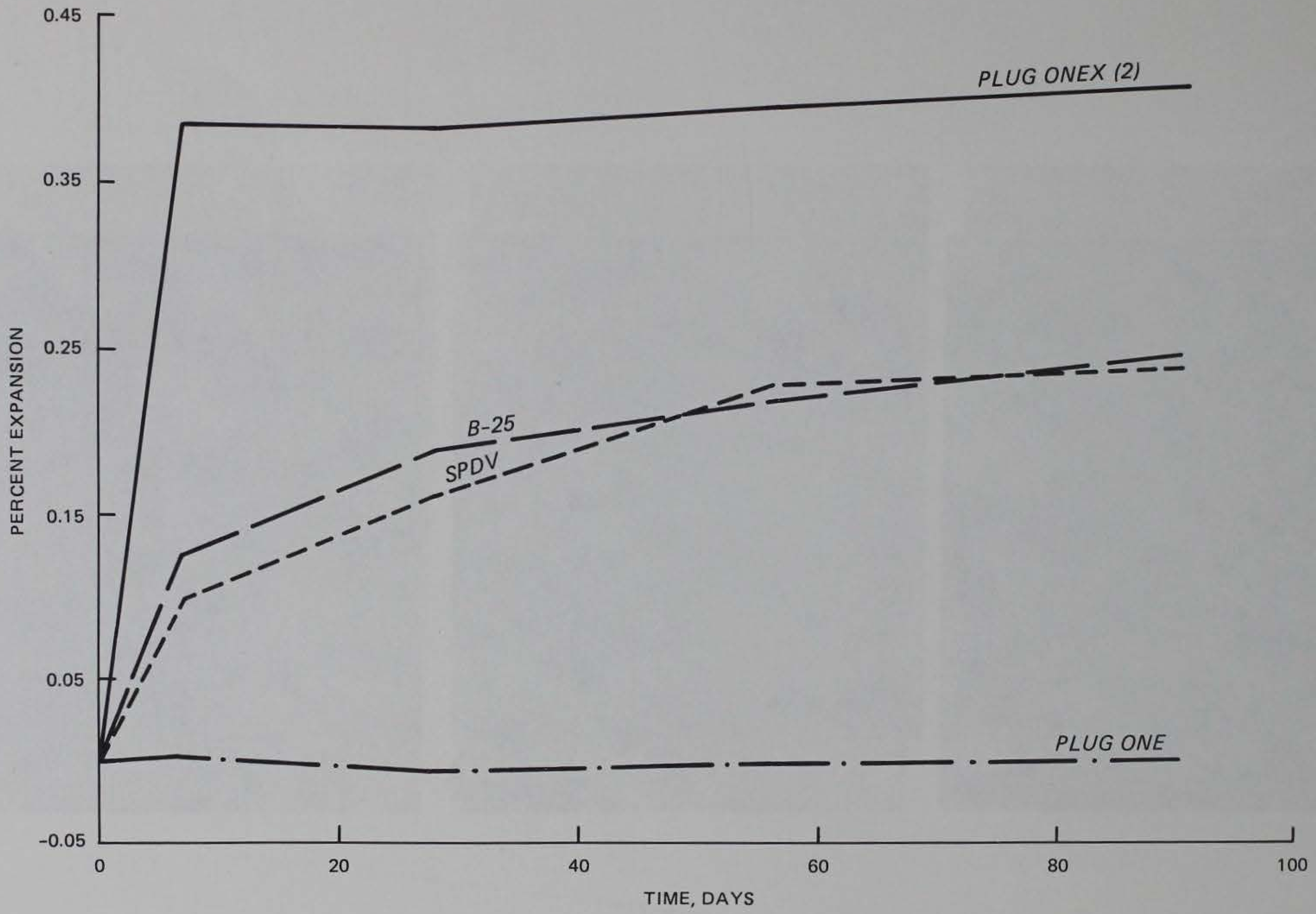

0.45
0.35
0.25
0.15
0.05
-0.05
PERCENT EXPANSION
0
20
40
60
80
100
TIME, DAYS
PLUG ONEX (2)
B-25
SPDV
PLUG ONE

Figure 3

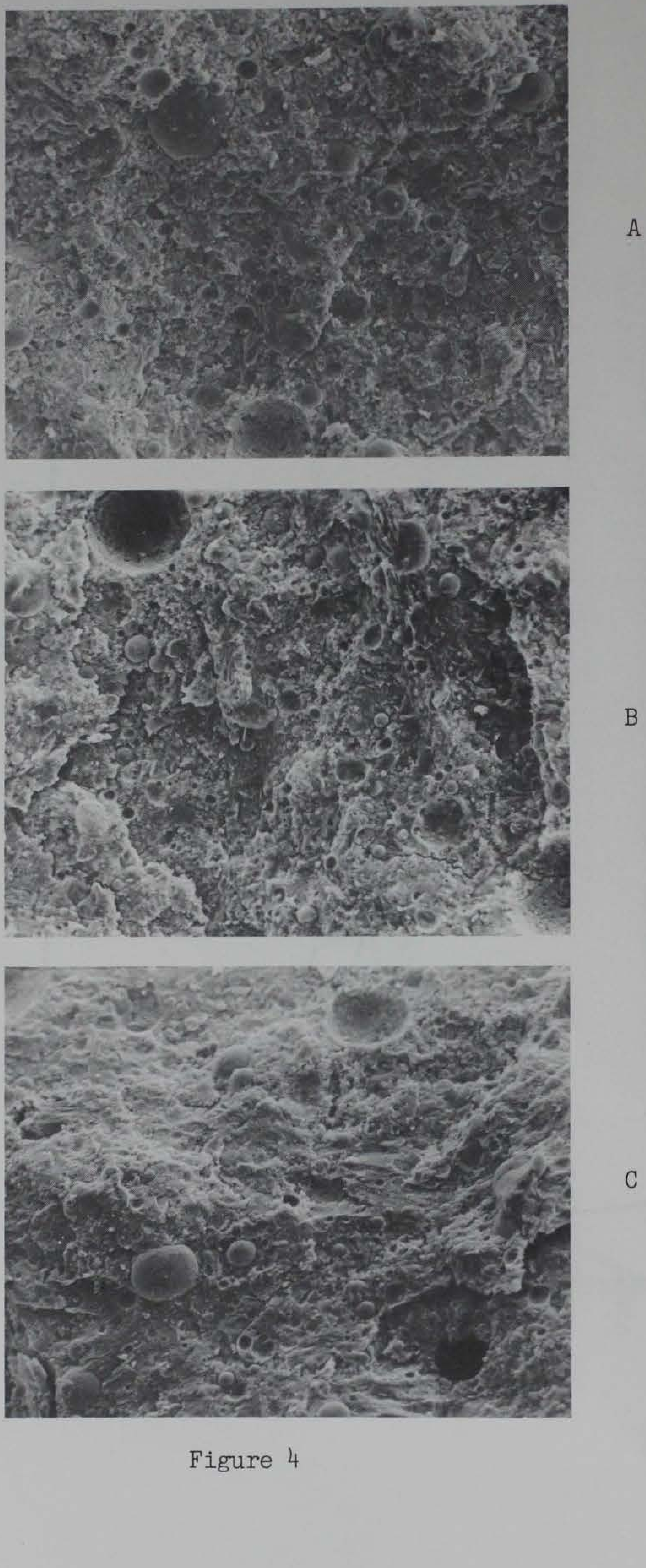


Figure 4

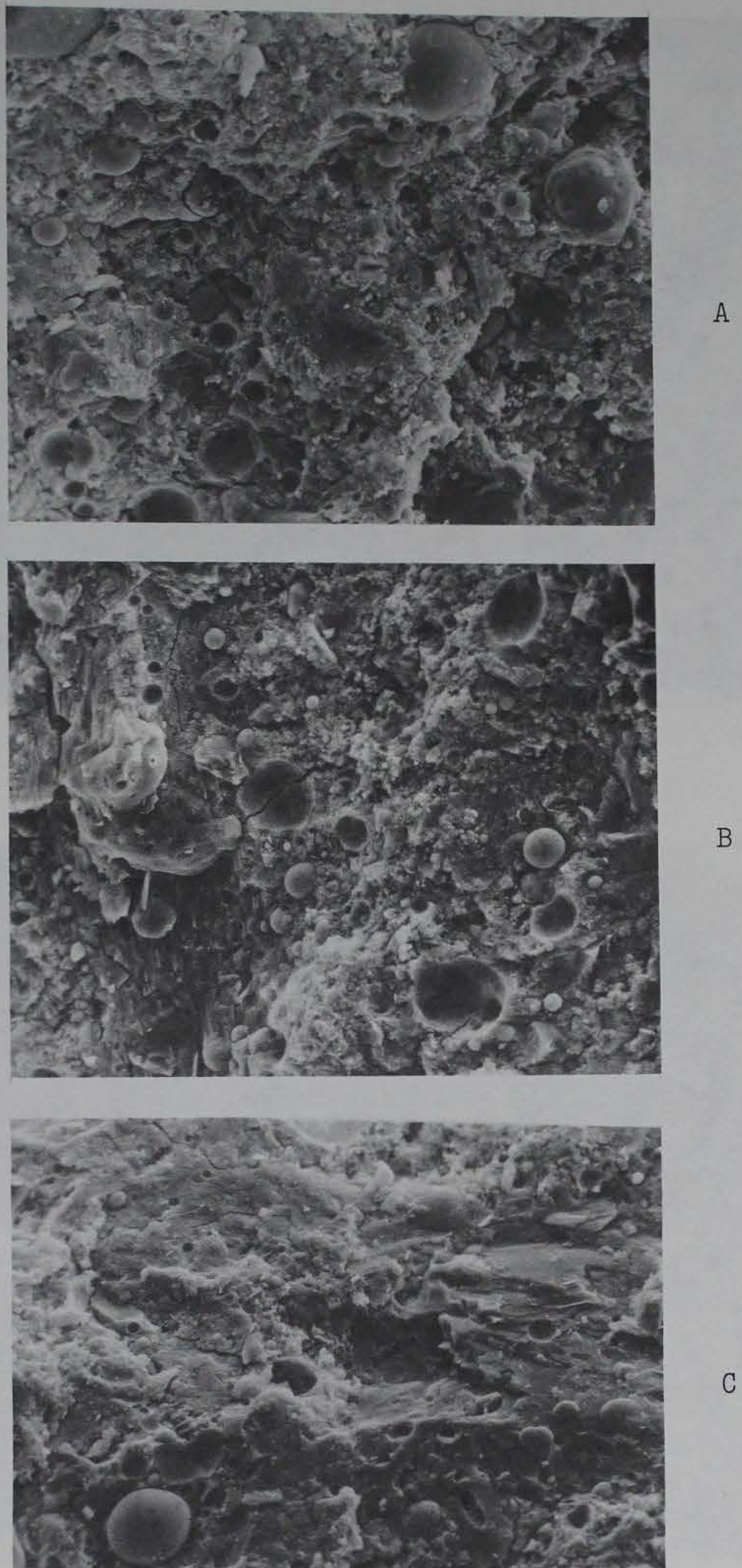


Figure 5

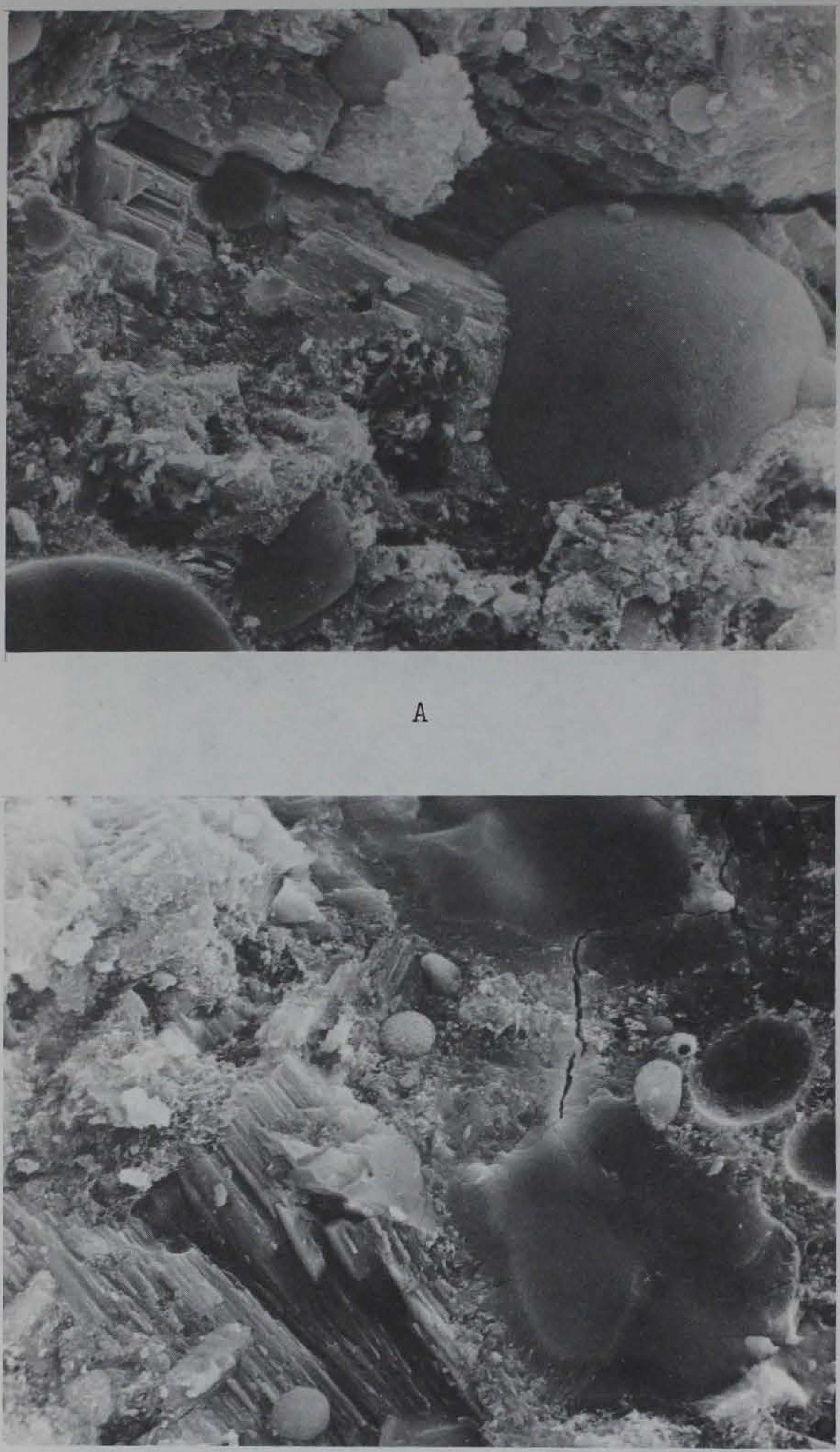
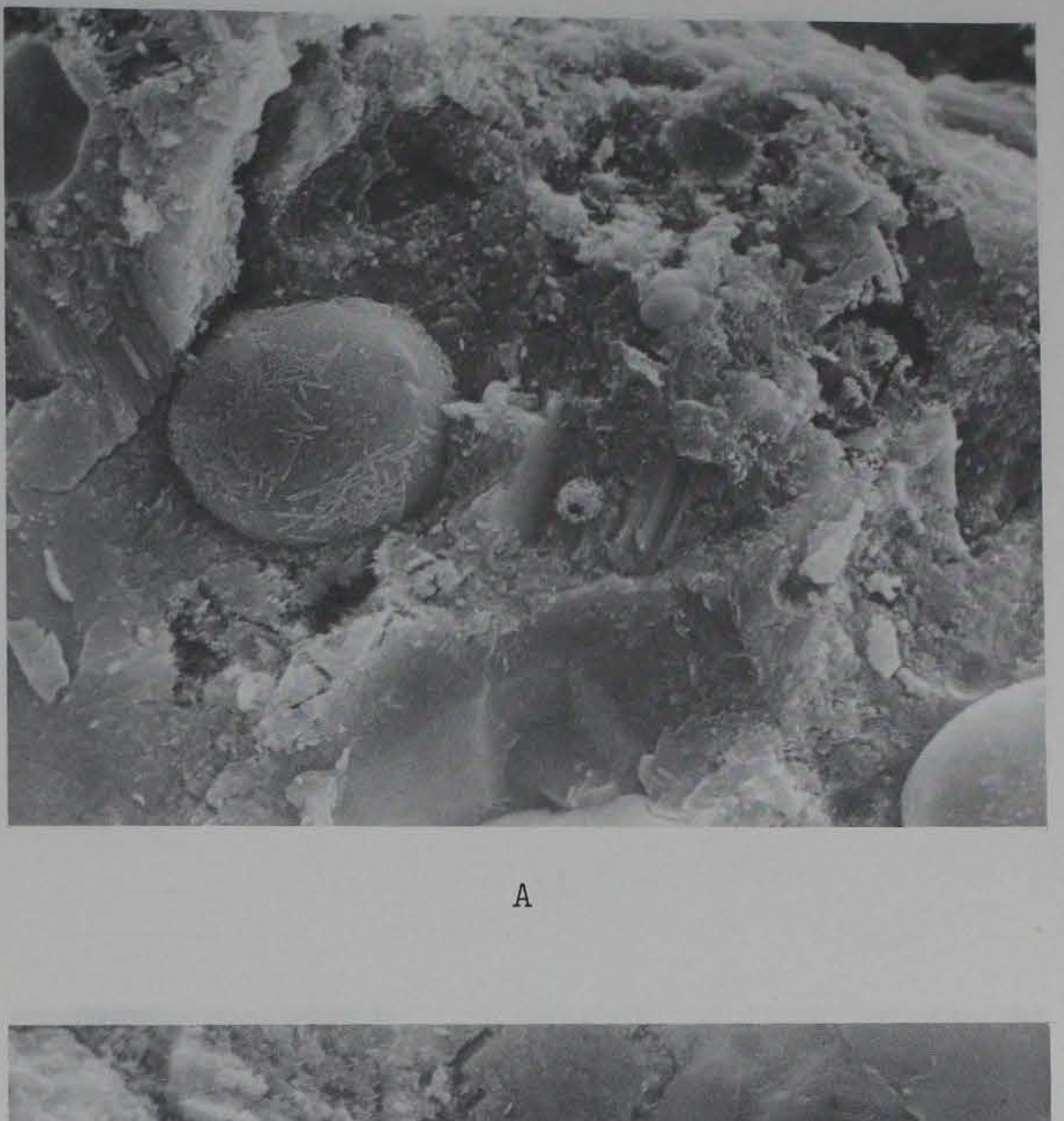


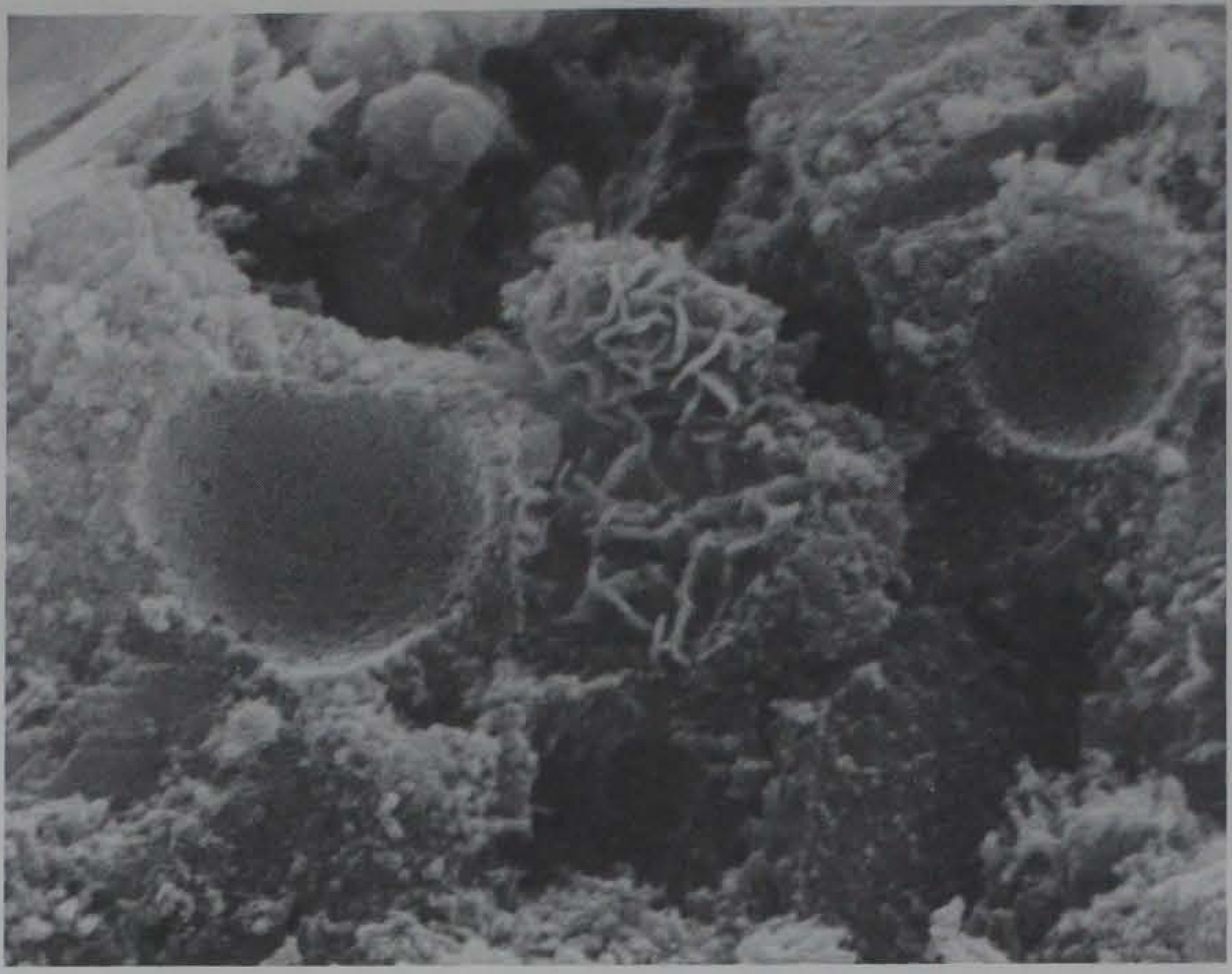
Figure 6



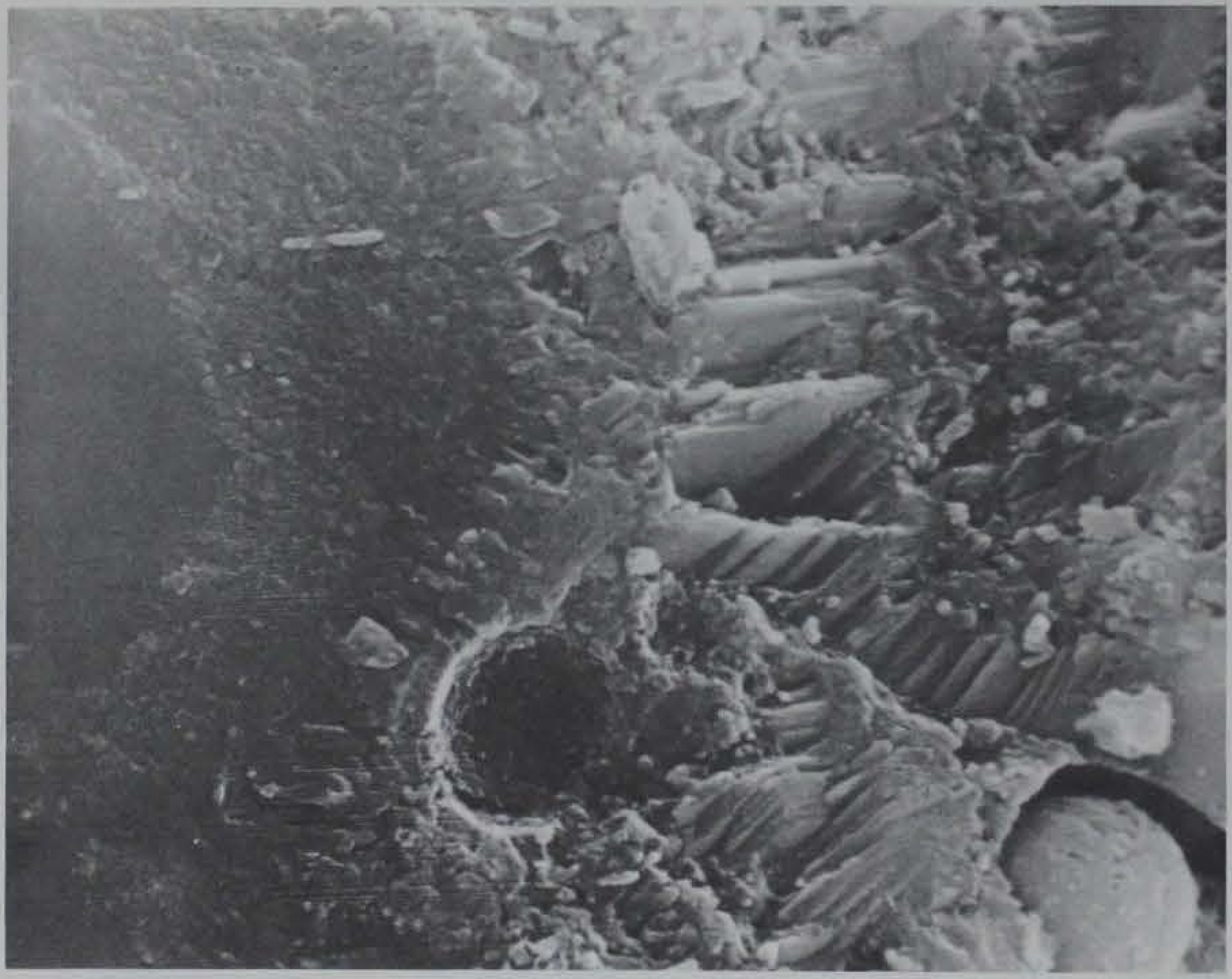
A

B

Figure 7

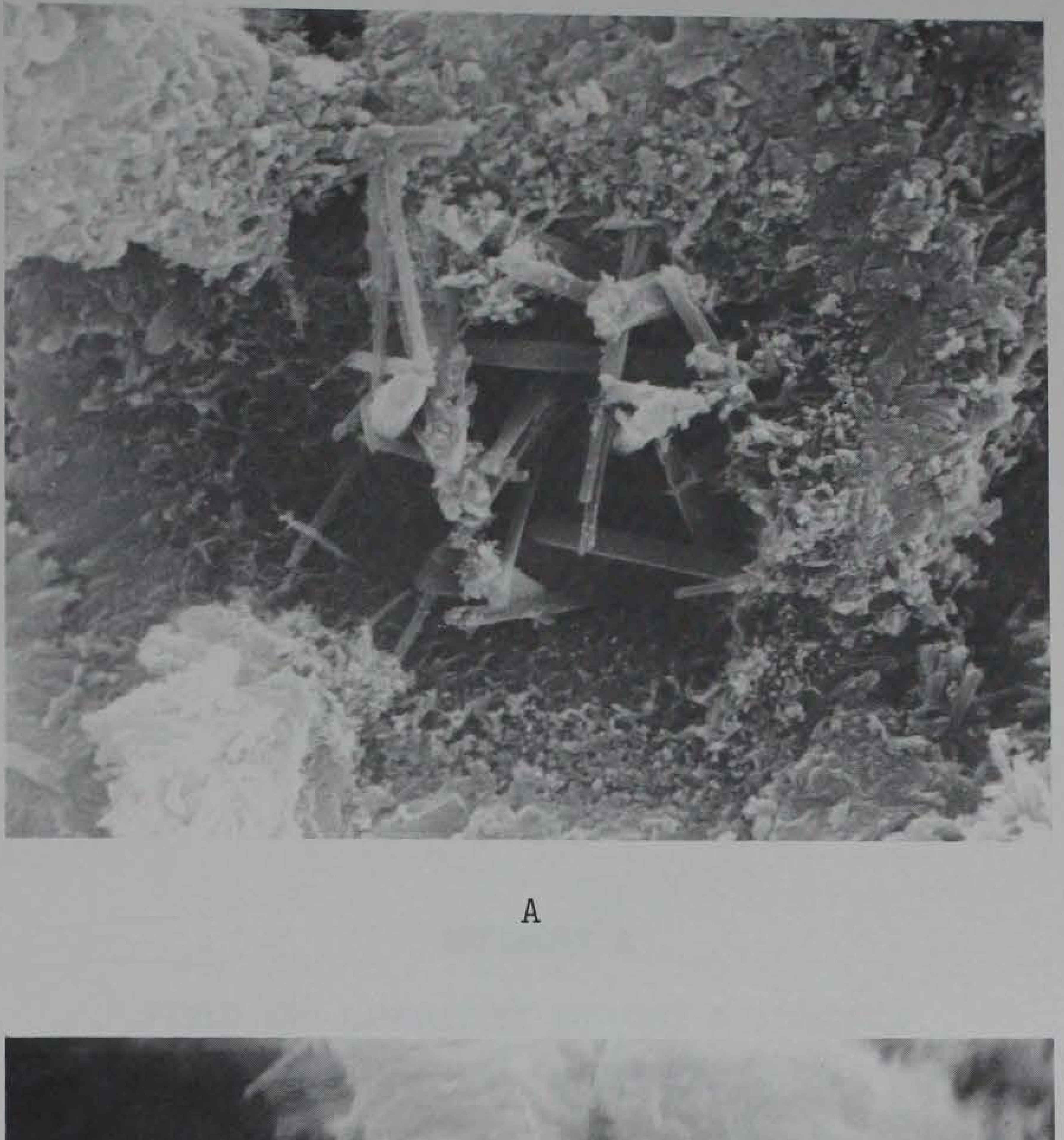


A



B

Figure 8



A

B

Figure 9

APPENDIX A

FIELD AND LABORATORY SUPPORT ACTIVITIES
OF SL-WES FOR WIPP GROUTING EVENTS

1. Participation in pre-placement meetings with agency and contractor personnel.

2. Visits to the placement site and contractor facilities prior to field operations.

3. Inspection of contractor batching, weighing, transport, and materials-storage facilities.

4. Developing and testing special equipment or procedures in the laboratory, for non-standard or new tests to be performed in the field.

5. Familiarization with contractor equipment and personnel procedures.

6. Assistance in siting storage, mixing, pumping, and quality-control equipment in the field, to ensure proper and timely placement.

7. Inspection of a field laboratory, to monitor placement at the field site.

8. Procuring samples of materials designated for field use, and shipping these to SL-WES for characterization and analyses as needed.

9. Monitoring grout mixing and fluid-state preperties during mixing and pumping operations. This includes checking mixing times, grout fluid weights, grout temperature, pumping rates, and pressures.

10. Casting of samples for laboratory tests during placement operations.

11. Maintaing proper curing conditions for field-cast specimens prior to shipment to WES.

12. Early-age testing of field-cast specimens before they are transported to the laboratory.

13. Packing and shipment of field-cast specimens to WES, and often to other laboratories.

14. Laboratory storage, under controlled environmental conditions, of field-cast specimens, for periodic testing of physical, mechanical, and microstructural properties, and monitoring long-term durability.

15. Laboratory testing, data analysis, and reporting.

APPENDIX B

MIXING AND PLACING TECHNIQUES

1. Field operations for mixing and placement of SPDV grout are similar to those described by Gulick, Boa, and Buck (1980). Batching and mixing were accomplished by a private contractor, under the general supervision of personnel of the SL Grouting Unit.

2. Fluid weight of the freshly mixed grout was checked frequently during placement, as were temperature, and pumping rates and pressures.

3. Filling the annulus between the steel pipe and the enclosing rock required four hours.

4. Specifications for the SPDV grout were as follows:

CEMENT: Class H oil well cement, with 30% volume replacement by class C fly ash

MINIMUM FLUID DENSITY: 17.5 lb/gal

WATER-CEMENT RATIO: 0.28 to 0.30 by mass

MINIMUM TIME GROUT REMAINED PUMPABLE: 3 hours

MAXIMUM VISCOSITY: 20 poise

MINIMUM EXPANSION: 0.1% at 28-days age

PERMEABILITY: <0.001 microdarcy

MINIMUM COMPRESSIVE STRENGTH: 10,000 psi @ 28 days

Additives as necessary. No high-density weighting materials or salt (NaCl) to be added.

APPENDIX C

CHEMICAL COMPOSITION AND DATA FROM PREPLACEMENT TESTING OF COMPONENTS OF SPDV GROUT

LABORATORY: Structures Laboratory Waterways Exp Station ATTN: Cem & Pozz Group P.O. Box 631 Vicksburg, MS 39180	REPORT OF TESTS ON POZZOLAN SS-C-1960/5 AD-677	REPORT NO.: WES-520F-81 SHEET 1 OF 1 DATE: 4 Jan 82

CLASS [✓ F] N — KIND OF POZZOLAN: Fly Ash

SOURCE: Trinity Mtls, Fairfield, TX — BRAND:

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

FOR USE AT:

CONTRACT NO.:

DISTRICT(S):

SAMPLED BY: — DATE SAMPLED: 18 Dec 81

CAR NO.: — BIN NO.:

FIELD SAMPLE NO.: — LAB SAMPLE NO.:

DATE RECEIVED: — LAB JOB NO.: 441-S864.22SC21

TESTED BY: Cement & Pozzolan 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							
86.1	1.8	0.1		*		0.00	

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 3
TEST RESULTS								
1	0.0	0.2	42 **		940	98	2.24	
Total	Alkali	as Na_2O,%:	0.85		SiO_2	%:	63.75	
					Al_2O_3	%:	19.45	
		~~Na_2O,%:~~	~~0.31~~		Fe_2O_3	%:	2.88	
		K_2O, %:	0.82		CaO	%:	8.35	
AVERAGE	—	—		—	—	—		—

(a) APPLICABLE ONLY TO CLASS N

(b) OPTIONAL REQUIREMENT

LABORATORY CEMENT USED Ideal, Tijeras, NM

LABORATORY LIME USED Chemstone

REMARKS: **Exceeds specification requirements for fineness. *28 day test results.

R. E. Reinhold

R. E. REINHOLD

Acting Chief, Cement & Pozzolan Group

TO:
Concrete & Grout Group
Structures Laboratory
ATTN: Don Walley

REPORT OF TESTS OF PORTLAND CEMENT

RC-881

FROM: CORPS OF ENGINEERS
U. S. ARMY
Structures Laboratory
Waterways Exp Station
ATTN: Cem & Pozz Group
P.O. Box 631
Vicksburg, MS 39180

TEST REPORT NO. WES-519-81 BIN NO. CAT REPRESENTED: DATE: 4 Jan 82
SPECIFICATION: Class H Oil Well DATE SAMPLED: 18 Dec 81
COMPANY: Lone Star LOCATION: Marvneal, TX BRAND:
THIS CEMENT DOES MEET SPECIFICATION REQUIREMENTS

SAMPLE NO.	1							
SiO_2, %	22.2							
Al_2O_3, %	3.5							
Fe_2O_3, %	3.6							
MgO, %	3.3							
SO_3, %	2.1							
LOSS ON IGNITION, %	0.1							
ALKALIES-TOTAL AS Na_2O, %	0.59							
Na_2O, %	0.16							
K_2O, %	0.65							
INSOLUBLE RESIDUE, %	0.50							
CaO, %	63.4							
C_3S, %	54							
C_3A, %	3							
C_2S, %	22							
$C_3A + C_3S$, %	58							
C_4AF, %	11							
$C_4AF + 2\,C_3A$, %	17							
HEAT OF HYDRATION, 7D, CAL/G								
HEAT OF HYDRATION, 28D, CAL/G								
SURFACE AREA, SQ CM/G (A.P.)	2300							
AIR CONTENT, %	13.7							
COMP. STRENGTH, 3 D, PSI	2180							
COMP. STRENGTH, 7 D, PSI	2730							
COMP. STRENGTH, D, PSI								
FALSE SET-PEN. F/I, %								
SAMPLE NO.	1							
AUTOCLAVE EXP., %	0.04							
INITIAL SET, HR/MIN	3:20							
FINAL SET, HR/MIN	6:50							
SAMPLE NO.								
AUTOCLAVE EXP., %								
INITIAL SET, HR/MIN								
FINAL SET, HR/MIN								

REMARKS: 441-S864.22SC21

CC: John Boa

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

R E Reinhold
R. E. REINHOLD
Acting Chief, Cement & Pozzolan Group

ENG FORM 1 MAR 72 6008-R

APPENDIX D

TEST METHODS FOR FLUID GROUT AND HARDENED SPECIMENS OF SPDV GROUT

D-1. FLUID GROUT

1. Flow: CRD-C 611-80, Method of test for flow of grout mixtures.

2. Time of setting: CRD-C 614-80, Meghod of test for time of setting of grout mixtures.

D-2. HARDENED GROUT

1. Compressional wave velocity: CRD-C 51-72, Standard method of test for pulse velocity through concrete.

2. Restrained and unrestrained expansion: CRD-C 225-76, Standard method of test for restrained expansion of expansive cement mortar.Standard test method was modified to include prisms of non-standard sizes. Unrestrained prisms were cast with end plates and caps for measurement, but without a threaded steel rod. Curing conditions were varied to determine the effect of different conditions on level of expansion (see text).

3. Permeability: CRD-C 48-73, Method of test for water permeability of concrete.

4. Compressive strength of cubes: CRD-C 227-80, Compressive strength of hydraulic cement mortars (using 2-in or 50-mm cube specimens).

5. Unconfined compressive strength: CRD-C 14-80, Compressive strength of cylindrical concrete specimens (modified by using grout specimens).

6. Dynamic modulus of elasticity: CRD-C 18-59, Method of test for fundamental transverse, longitudinal and torsional frequency of concrete specimens (used for grout).

7. Static modulus of elasticity: CRD-C 19-75, Standard method of test for static modulus of elasticity and Poisson's ratio of concrete in compression (used for grout).

8. Porosity, oven-dry density, and crushed-grain density: T-1 Method, Reference Method Appendix IV, US Army Engineering Manual (EM) 1110-2-1906, Laboratory Soils Testing (30 Nov 70).

9. Bond strength: Special test method to measure bonding of hardened grout to steel. A column of fluid grout is allowed to harden in a length of steel pipe. The force necessary to dislodge the hardened grout from the area in contact with the pipe indicates bond strength, and indirectly indicates expansion or shrinkage.