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PETROGRAPHIC EXAMINATION OF BELL CANYON TESTS (BCT) 1-FF FIELD GROUTS OVER A THREE-YEAR PERIOD

by

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The Bell Canyon field test involving the placement of two grout plugs took place 26 September 1979 (Plug 1) and 14 February 1980 (Plug 2), respectively. Samples cast in the field were brought to WES and cured in hole AEC-7 (lease) brine. Samples were examined periodically through 1 year and then at 2- and 3-years age to obtain petrographic, physical, and some chemical data. This report deals solely with the petrographic data as the physical data have been presented

(Continued)

20. ABSTRACT (Continued)

in other reports. Cracking of specimens was observed; this was believed to be due largely to moisture and temperature changes in the laboratory.

The two plugs were similar in composition with the Plug 1 grout having more tetracalcium aluminate monosulfate-12-hydrate ($C_4A\bar{S}H_{12}$) and more garnet-hydrogarnet solid solution series material (hydrogarnet) by X-ray diffraction (XRD) than Plug 2. Tetracalcium aluminate dichloride-10-hydrate ($C_3A(CaCl_2)H_{10}$ was present in both samples in varying amounts at different ages. The amount of $C_3A(CaCl_2)H_{10}$ in the samples was probably controlled by the proximity of the surface examined by XRD to the brine the samples were stored in.

The Plug 2 grout contained more ettringite and calcium hydroxide; Plug 1 grout contained more detectable calcium silicate hydrate (C-S-H). The grout to host anhydrite rock bond appeared to be tight with no visible cracking in simulated borehole (SBH) samples that were examined immediately after fracturing. A white precipitate was found on samples of both events during storage and is believed to be a combination of some chemical reaction between the groundwater and grout as well as precipitate from the brine. It had no detectable detrimental effects.

The infiltration of the brine during placement of the grout in satellite Holes 3 and 4 weakened the grout and retarded some of the grout so that it did not harden.

The XRD examinations of both Plug 1 and Plug 2 grouts point out that chloride and carbonate ions from the brine are causing some alteration to the original phases at and near the contact of grout and brine. After 3 years of storage, this alteration has penetrated the grout to a depth of about 1 or 1.5 in. with the severity of alteration becoming less with increasing distance from contact surfaces.

The grout from the two placements at ages up to 3 years showed no significant overall deterioration or alteration from the original grout.

The Plug 1 and Plug 2 samples will continue to be examined by XRD and SEM at 1-year intervals for an indefinite time.

PREFACE

This report describes work done for the U. S. Department of Energy under contract DE-AI97-81ET 46630 and modifications thereto. Messrs. Floyd Burns and Lynn Myers, Office of Nuclear Waste Isolation (ONWI), Battelle Memorial Institute, Columbus, Ohio, were earlier Project Managers. Mr. Don Moak is the present Project Manager. Sandia National Laboratories used the BCT 1-FF grout mixture for their Bell Canyon Tests in southeastern New Mexico as part of their Plugging and Sealing Program. The Concrete Technology Division (CTD) of the Structures Laboratory (SL) of the U. S. Army Engineer Waterways Experiment Station (WES) provided field support. Mr. Bryant Mather is Chief of the SL and Mr. John M. Scanlon, Jr., is Chief of the CTD.

Periodic petrographic examination of field specimens was done in the SL under the direction of Mrs. Katharine Mather, Project Leader at that time. Mr. Alan D. Buck is now the Project Leader. Messrs. Jay E. Rhoderick and Jerry P. Burkes generated the petrographic data and analyzed them. Mr. Rhoderick prepared the original draft of the report through one year of testing. Mr. Burkes combined the later results into a revision of the whole report.

COL Nelson P. Conover, CE, was Commander and Director of WES when this work began. COL Tilford C. Creel, CE, is the present Commander and Director. Mr. F. R. Brown was Technical Director.

CONTENTS

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

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

Multiply	By	To Obtain
Fahrenheit degrees	5/9	Celsius degrees*
feet	0.3048	metres
inches	25.4	millimetres
pounds (force) per square inch	6.894757	kilopascals

* 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 = C + 273.15.

PETROGRAPHIC EXAMINATION OF BELL CANYON TESTS (BCT) 1-FF FIELD GROUTS OVER A THREE-YEAR PERIOD

PART I: BACKGROUND

1. Field studies play a key role in the development of cementitious sealing formulations for use in and around nuclear waste repositories. These studies provide realistic input parameters for seal design and are intended to demonstrate the validity of predicted behavior of a seal design and sealing material as determined during laboratory testing.[1] The first significant planned field test sponsored by the U. S. Department of Energy (DOE) has been the Bell Canyon Test (BCT). This involved the placement of two grout plugs in the existing borehole AEC-7 at the Los Medanos site in New Mexico. The plugs were placed in anhydrite host rock at a depth of approximately 4000 ft.* The first plug was cast 26 September 1979 and was approximately 6 ft long. The second plug was cast 14 February 1980 on top of the first plug and was approximately 12 ft long. A large number of expansion prisms, simulated borehole (SBH) samples, cylinders, and cube specimens were also cast in the field at time of placement to provide physical properties and petrographic samples of the same grout that was placed in the borehole. All of these samples were taken to the Structures Laboratory (SL) for storage in brine groundwater from hole AEC-7 and periodic testing. The handling and curing information for these specimens has been reported.[2] Specimens representative of the grout in each plug were selected for periodic examination by X-ray diffraction (XRD) to study phase composition of the grout. Examination by scanning electron microscopy (SEM) was added at a later date to study microstructure. Examinations of other samples were made for other purposes and are included herein for the purpose of consolidating this information into one report.

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

PART II: SAMPLES

2. Various samples that were representative of Hole AEC-7 Plug 1 and Plug 2 grout or of this grout mixture or of the hole were received and examined. They included:

Sample Identification	Date Received	Description	Instrumentation Used for Examination
A4	11 October 1979	Plug 1 grout, 2-in. by 2-in. by 2-in. unbroken compressive strength cube. Miscellaneous pieces of cylinders were also used.	X-ray diffraction (XRD), scanning electron microscope (SEM), stereomicroscope.
A5	17 October 1979	Plug 1 soft, unset grout from satellite Hole 3 of AEC-7, taken 2 ft from top of plug	XRD, stereomicroscope
A6	17 October 1979	Plug 1, soft unset grout from satellite Hole 3 of AEC-7, taken from top of plug	XRD, stereomicroscope
A8	30 November 1979	Plug 1 grout, simulated borehole (SBH) sample, tested for permeability	Stereomicroscope
A9	3 December 1979	Plug 1 grout, SBH sample, tested for permeability	Stereomicroscope
A11	3 April 1981	Plug 1 grout from top of satellite Hole 4 of AEC-7	XRD, stereomicroscope
A12	3 April 1981	Plug 1 grout from bottom of satellite Hole 4 of AEC-7	XRD, stereomicroscope
CL-30 W-3	9 December 1980	1 gal 10 lb brine from Hole AEC-7 taken at time Plug 2 was placed	Wet methods, atomic absorption spectrometer (AA)
CL-30 W-5	24 March 1980	Plug 2, black sludge from location of plug prior to plug placement	XRD, AA
CL-30 GRT-57	25 March 1980	Plug 2, SBH sample	Stereomicroscope

Sample Identification	Date Received	Description	Instrumentation Used for Examination
CL-30 GRT-158	9 April 1980	Plug 2 grout, 2-in. by 2-in. by 2-in. unbroken compressive strength cube. Miscellaneous pieces of cylinder were also used.	XRD, SEM, stereomicroscope
Unnumbered	23 April 1980	Plug 1 grout, white precipitate found on cylinders	XRD, AA, stereomicroscope
Unnumbered	24 March 1980	Plug 2 dry mixture of BCT-1-FF from NTS-Dowell Batch Plant, sampled 13 February 1980	XRD
Unnumbered	25 March 1980	Plug 2 high-strength broken NX core from a cylinder	XRD, SEM

The above listing is generally by sample or serial number, not by testing sequence. The samples may also be grouped as follows:

a. Slices from cylinder fragments or cubes A4 (Plug 1) and CL-30 GRT-158 (Plug 2) were examined periodically for 1 year and at 2-year and 3-year ages for phase composition by XRD; they were also examined at 1-, 2-, and 3-year age for microstructure by SEM. In addition, an NX core that was drilled from a 6-in. cylinder of Plug 2 grout and tested for compressive strength at about 15-months age was examined by XRD and SEM.

b. Brine (CL-30 W-3) taken from Hole AEC-7 at the time the second plug was placed to establish its composition.

c. The sample of black sludge (CL-30 W-5) from Hole AEC-7 was examined between placement of the two plugs to verify that Plug 1 was not being attacked by an aggressive environment.

d. White precipitate forming on specimens during storage in brine in the laboratory was examined to determine its source.

e. Three SBH samples (A8, A9, CL-30 GRT-57) were examined to determine the quality of contact of the BCT-1-FF grout and anhydrite rock. Samples A8 and A9 were examined after they leaked during permeability testing. Sample CL-30 GRT-57 was examined when it cracked before testing.

f. Samples A5 and A6 from Plug 1 satellite Hole 3 were examined when the grout was 22 days old. Samples A11 and A12 from Plug 1 satellite Hole 4 were examined when the grout was about 19 months old. The satellite holes consisted of plastic tubes (~6-in. diameter) about 20 ft long embedded near the AEC-7 hole. Sand was placed in the bottom of them and they were filled with the brine from Hole AEC-7. They were then filled with grout to somewhat simulate the actual placement of the Plug 1 grout in Hole AEC-7.

g. The unnumbered sample of the BCT-1-FF grout mixture without any water being added was examined to determine which components were detectable by X-ray diffraction.

3. In addition, six samples representing three types of Plug 2 specimens were sent to Dr. Della Roy at the Materials Research Laboratory of the Pennsylvania State University about 21 March 1980. They were as follows:

a. Two SBH samples (CL-30 GRT-54 and 62).

b. Two 6- by 12-in. cylinders of grout cast in plastic molds when the grout was about 1 hr old (CL-30 GRT-95 and 96).

c. Two 3- by 6-in. cylinders of grout cast in steel molds (CL-30 GRT-107 and 108).

PART III: EXAMINATIONS

Cracking

4. All of the AEC-7 Plug 1 and Plug 2 samples were inspected when they were about 12 to 18 months old and at 2- and 3-years age for the presence of cracking or other distress. These specimens were not those listed above.

Periodic XRD and SEM Examinations

5. Samples A4 and CL-30 GRT-158 were the ones used to identify the composition and changes in composition with increasing age of the grout like that in each plug. Both samples were prepared and examined in the same way. Slabs 1/4 in. thick by 1 in. wide by 2 in. long were used for the XRD examination and came from 2-in. by 2-in. by 2-in. cubes or from pieces of cylinders. The specimens were ground in methanol until the saw marks were gone. This smoothed surface was examined by XRD in an environment of static nitrogen gas with a hot beaker of saturated barium hydroxide solution or a sponge saturated with it. Portions of sample A4 were examined by XRD at 15-, 28-, 56-, 98-, 180-, and 370-days and 2- and 3-years age. Portions of sample CL-30 GRT-158 were examined by XRD at 55-, 90-, 180-, and 370-days and 2- and 3-years age. An NX core that was removed from a 6-in. cylinder of Plug 2 at about 15-months age had especially high strength (25,000+ psi); it was examined by XRD and SEM for phase composition and microstructure. The XRD sample was a tightly packed powder in a 3-in. aluminum holder. When it was decided to include SEM examination of Plug 1 and Plug 2 samples, the pieces that had been examined by X-ray diffraction at 370-days age were used. They had been kept in methanol in a freezer since that time. Therefore, the SEM specimens were simulations of 370-days age. It is believed that the storage conditions used effectively inhibit change in composition or microstructure with time. The 2- and 3-year old SEM specimens were examined at the time XRD examinations were done. The SEM samples were placed

in a vacuum desiccator in an oven at about 50° C with a mechanical vacuum pump attached. They were left in the vacuum for approximately 16 hr. The samples were then fractured in a plane parallel to the plane examined by XRD and then placed in a vacuum evaporator and subjected to further evacuation as needed before coating with a 5-nm layer of carbon followed with a 15-nm layer of a gold-palladium alloy (80:20) to make the samples electrically conductive.

AEC-7 Brine

6. The sample (CL-30 W-3) was characterized by AA and wet methods of analysis.

Black Sludge

7. The black sludge (CL-30 W-5) was examined by XRD and atomic absorption (AA) and has been reported elsewhere.[2]

White Precipitate

8. The white precipitate found on both Plug 1 and Plug 2 specimens during storage was scraped from several 6- by 12-in. Plug 1 cylinders and from sample CL-30 GRT-158 and placed on glass slides as a slurry. After drying, they were examined by XRD. Some of it was also examined by AA to determine its magnesium content.

Simulated Borehole (SBH) Samples

9. Sample A8 was tested for permeability for 4 days using nitrogen gas. It was then tested for permeability using fresh water. After permeability tests were completed, the sample was placed in a plastic bag and stored at 73° F for approximately 45 days until petrographic examination was done. Sample A9 was also tested using both nitrogen gas and fresh water for permeability. Four slices, two from the top and two from

the bottom, of the sample were examined. The Samples, A8 and A9, were examined by visual inspection and with the aid of a stereomicroscope. The steel retaining ring and outer ring of grout were removed from both samples prior to fresh water permeability testing. Sample CL-30 GRT-57 was broken for petrographic examination. A portion from the top and bottom was obtained by using a pipe cutter to cut the metal ring before breaking across the SBH sample. The broken surface was examined using the technique developed for examination of SBH samples.[3]

Satellite Holes 3 and 4

10. Samples A5 and A6 from satellite Hole 3 were examined by visual inspection and by observation with a stereomicroscope. A portion of each sample was ground and examined by XRD in an environment as before. Samples A11 and A12 from satellite Hole 4 were examined by visual inspection and by XRD. A sample from the top and bottom of A11 and from the top of A12 was ground and examined as a tightly packed powder by XRD in the same environment as before.

Dry Batched BCT-1-FF

11. A dry mixture of the BCT-1-FF grout used in Plug 2 was examined by XRD as a tightly packed powder in an environment of static nitrogen gas.

12. All the X-ray work was done with an X-ray diffractometer using nickel-filtered copper radiation.

PART IV: RESULTS

Cracking

13. Cracking was found in samples representing both plugs. Five types of cracking and deterioration were seen. They were: longitudinal, cross, diagonal (all relative to the long axis orientation), spalling, and arch cracking. Deterioration was more prevalent in the larger size samples. The types of samples and the cracking found in those samples are listed in Table 1. A 3-in. by 3-in. by 10-in. unrestrained prism representative of each plug (sample 2C, Plug 1, and sample CL-30 GRT-6, Plug 2) broke along a cross fracture during handling. This is shown for prism CL-30 GRT-6 by Figure 1. The cracking is believed to be due to normal volume change induced by temporary drying and temperature change (100^{o} F to 73^{o} F) of high cement content and no aggregate restraint of grout during testing of the samples.

Periodic XRD and SEM Examinations

14. Table 2 lists the detectable crystalline phases found by XRD in Plug 1 (A4) and Plug 2 (CL-30 GRT-158) samples through 3 years of testing. Ettringite was abundant in both samples at all ages and the 3-year-old specimens probably contained more ettringite than specimens at any other age. Although both samples still contain unhydrated portland cement at 3 years, the amount is decreasing as the samples grow older. The Plug 2 sample had more of most crystalline phases that were present in the samples with the exception of C-S-H,* which is a poorly crystalline compound, than Plug 1. Plug 1 contained more C-S-H. The Plug 1 specimens at 180-days and at 1-year ages had no detectable calcium hydroxide (CH). At both these ages the $C_3A(CaCl_2)H_{10}$ XRD peak with a spacing of 7.80A to 7.90A** was quite strong. Also, the XRD pattern of the 370-day-old

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* Usual cement notation where: C = CaO; A = Al_2O_3; H = H_2O; $\overline{S}$ = SO_3; $\overline{C}$ = CO_2.

** A x 10^{-1} equals nanometres.

sample contained some gypsum. The 2-year-old specimen from Plug 1 did not show any $C_3A(CaCl_2)H_{10}$ while the 3-year-old specimen contained a trace. Gypsum was not found in either sample and CH was a constituent in both samples. This seems to suggest that CH in this particular case was affected more strongly than ettringite by the formation of $C_3A(CaCl_2)H_{10}$. By 2 years the amount of CH seemed to be about the same in both samples; however, at 3-years age, the amount of CH in Plug 2 was probably greater than the amount in Plug 1. Hydrogarnet was present in Plug 1 grout throughout the first 3 years. The Plug 2 grout did not show hydrogarnet until it was 2 years old. Hydrogarnet was tentatively identified in the 3-year-old specimen of Plug 2 grout and the high-strength NX core at 15-months age. The presence of hydrogarnet in the Plug 1 sample at its younger ages was probably due to the higher temperature it was subjected to during the first 24 hr after casting.

15. The 15-month-old high-strength NX core that was removed from a 6-in. cylinder of Plug 2 grout contained the same phases by XRD as this grout did at other ages with the exception of $C_3A(CaCl_2)H_{10}$, which was absent. The core was removed from the center of the cylinder. The absence of $C_3A(CaCl_2)H_{10}$ indicated that chloride ions had not permeated the cylinder to the area where the NX core was taken by 15-months age. Direct comparison of amounts of phases between the high-strength core and other grout of about this age from this plug was not feasible since the core was examined as a ground powder and the others as slabs. Therefore, comparison was by SEM. Comparison of microstructure in the appropriate samples by SEM (Figures 7, 14) did not indicate significant differences, but SEM did show the dense microstructure expected of this high-strength material. Nine SEM micrographs are shown in Figures 6 through 14 of Plug 1 and Plug 2 grout. They show a microstructure that is normal for this material. Comparison of Figures 7 and 14 with Figure 6, all at about 500 X, suggest a slightly denser microstructure for the Plug 2 grout. It has been observed that comparison of fracture surfaces of such micrographs at about 200 or 500 X is useful since there seems to be a correlation between smoothness of break and increased strength. Such a comparison is shown by Figures 6 and 7 with the Plug 2

grout fracture surface at about 1 year appearing smoother and thus stronger (denser). Figures 12 and 13 show the microstructure of the Plug 1 and Plug 2 grouts at 3 years age; the Plug 2 grout still shows a slightly denser microstructure than the Plug 1 sample does; however, it is not as apparent as it was at 370 days. Unhydrated grains of portland cement can be seen in both the micrographs of the 3-year-old grout. This suggestion of some difference in the grout of the two plugs is somewhat verified by the physical data through 130 days, especially the dynamic modulus, on page 60 of Reference 2.

16. Figure 14 shows the microstructure of the NX core grout that had 25,000+ psi strength. The core was Plug 2 grout and its microstructure is very similar to the Plug 2 grout at 370-days age.

17. The cracks seen in some of the micrographs are believed to be caused by the SEM preparation technique.

AEC-7 Brine

18. The chemical analysis of brine CL-30 W-3 is shown in Table 3. It has the sort of composition to be expected of such material.

Black Sludge

19. Examination of the black sludge, CL-30 W-5, from hole AEC-7 showed it to consist of rock and metal debris from the hole. Therefore, it was concluded that the grout of Plug 1 was not being attacked by its environment. These results were published earlier in Reference 2 (pp 65 through 68).

White Precipitate

20. A white precipitate on Plug 1 grout cylinders was examined by XRD at approximately 7-months age. Similar white material was also found on Plug 2 samples (Figure 2). The material on the surface of cube CL-30 GRT-158 was examined at an age of about 1 year. Both of these samples

of white precipitate contained brucite, gypsum, and salt (NaCl). A partial chemical analysis of this material from the Plug 1 cylinder showed it to contain 21.2 percent magnesium. The fact that the white precipitate was found only on grout and not on the anhydrite rock on SBH sample surfaces suggests some reaction between grout and brine water. However, considering the composition of the material, it is believed that the material precipitated out of the brine water and onto the sample surfaces as some evaporation took place and the brine became supersaturated.

Simulated Borehole (SBH) Samples

21. Samples A8 and A9 leaked in both gas and water permeability testing to the extent that no measurements were made. These samples were examined with a stereomicroscope. No continuous crack at the interface contact was detected in either sample. However, intermittent cracks were found along the interface areas. Cracks perpendicular to the contact of anhydrite to grout were found in the anhydrite. The removal of the steel retaining ring has been found to cause this type of cracking in SBH samples.[3] However, leakage during gas permeability indicates that these cracks may have been present before the removal of the steel ring. Examination of untested SBH samples that have been kept inundated in brine groundwater at 100^{o} F revealed that these samples also had cracking in the anhydrite. It is not known whether the anhydrite in samples A8 and A9 was cracked before or after the steel ring was removed.

22. Sample CL-30 GRT-57 was examined with a stereomicroscope at 40-days age. No cracks along the contact of grout to anhydrite were seen. A white halo was visible at the interface on both the top and bottom surfaces. Cracks in the anhydrite perpendicular to the interface were present. These cracks were probably caused by not having enough anhydrite thickness to resist the pressure exerted by the expansive grout plug.

Satellite Hole 3

23. Samples A5 and A6 from satellite Hole 3 contained ettringite, $C_3A(CaCl_2)H_{10}$, tetracalcium aluminate hemicarbonate-12 hydrate ($C_4A\overline{C}_{0.5}H_{12}$), C-S-H, gypsum, halite, and unhydrated portland cement. Calcium hydroxide (CH) was in sample A5 but not in sample A6. The $C_4A\overline{C}_{0.5}H_{12}$, $C_3A(CaCl_2)H_{10}$, and gypsum phases comprise a higher percentage of sample A6 than they do A5. Also, A6 has much less ettringite than A5 and as already mentioned, no CH. These XRD results indicate that the three phases, gypsum, $C_4A\overline{C}_{0.5}H_{12}$, and $C_3A(CaCl_2)H_{10}$ are forming at the expense of ettringite and CH. Judging from the XRD patterns of both samples, the C-S-H phase is probably about the same in both samples. The appearance, failure to set, and composition of the grout plus the fact that both these samples had to be dried before they could be prepared for XRD examination suggest that the brine in satellite Hole 3 effectively increased the water to solids ratio enough to cause the grout to fail to set and not to gain strength.

Satellite Hole 4

24. Samples A11 (0.8 ft long) and A12 (1.1 ft long) from Plug 1 satellite Hole 4 were examined visually for any defects; also, both samples were examined by XRD to determine the crystalline phases that were present. Two portions of specimen A11 were examined by XRD. One came from the top and the other from the bottom of the sample. Sample A12 came from 8.9 ft below the top of satellite Hole 4.

25. The A11 grout was soft and mushy on top and gradually hardened with depth. Discoloration caused by the infiltration of brine was visible on the outside of the sample to a depth of 0.3 ft. Cross, longitudinal, diagonal, and half-moon cracking were also visible on the surface of sample A11. The mottled discoloration caused by the brine combining with the grout mixture was seen through the center of sample A11 (Figure 3). XRD examination of the two samples from the A11 grout showed ettringite, $C_3A(CaCl_2)H_{10}$, $C_4A\overline{C}_{0.5}H_{12}$, CH, C-S-H, and halite to be common to both

samples. The sample from the top of the hole contained more $C_4A\bar{C}_{0.5}H_{12}$ and less CH than the bottom sample. Also, the top sample contained gypsum but the bottom sample did not. The sample from the bottom of A11 contained a trace of tetracalcium aluminate monosulfate-12 hydrate ($C_4A\bar{S}H_{12}$), but none was detected in the top material. The top of sample A12 showed intrusion of sand throughout the middle of the sample. There was also some mottling and discoloration in some areas (Figure 4). Sand from the bottom of the hole was mixed into the grout by turbulence during placement of the grout by the dump bailer (Figure 5). Longitudinal, cross, and diagonal cracking was found in the sample. A tan section ran longitudinally along A12 and is believed to be a carbonated area due to air trapped along the side of the hole. The phase composition of sample A12 and the bottom of sample A11 was similar by XRD except that A12 did not contain halite and had only a trace of $C_3A(CaCl_2)H_{10}$. The amount of $C_4A\bar{S}H_{12}$ in A12 and the bottom of A11 was about the same. All three samples contained ettringite, calcium silicate hydrate (CSH), quartz from the fly ash, and some unhydrated cement. The grout from satellite Hole 4 was about 19 months old whereas that examined from satellite Hole 3 was only 22 days old.

Dry Batched BCT-1-FF

26. The dry mixture of BCT-1-FF contained portland cement, calcium sulfate hemihydrate, and quartz by X-ray diffraction. These phases were expected and their quantities as indicated by X-ray diffraction were in general agreement with the grout mixture proportions. In addition to the above, lime (CaO) and periclase (MgO) were tentatively identified in the mixture; these two phases may be constituents of the fly ash.

PART V: CONCLUSIONS

27. Examination of grout samples cast in the field at the time grout Plugs 1 and 2 were placed in Hole AEC-7 and of associated samples has shown the following:

- a. Cracking of samples during storage in the laboratory was common. It is believed this was due to normal response of high cement content specimens to unavoidable small changes in temperature and/or moisture content. It is not believed that similar changes would occur in the actual plugs where temperature and moisture conditions would be more uniform. The addition of some aggregate to future grouts to provide some restraint against such cracking might be a useful precaution.

- b. The phase composition and microstructure of the grout representing the two plugs were normal for the ages examined. There was a normal increase in hydration products and decrease in unhydrated cement with time. This monitoring of phase composition and microstructure should be continued as an indication of what is happening to the plugs and as a measure of longevity of this material.

- c. The black sludge from Hole AEC-7 was normal rock and metal debris and was not grout from Plug 1. This showed that the grout was not being attacked by its environment.

- d. Soft white precipitation found on all specimen surfaces during laboratory storage in brine from Hole AEC-7 was due to evaporation of this water and subsequent precipitation on specimen surfaces and probably to some chemical reaction of the grout with the brine; this reaction did not appear to be harmful to the grout.

- e. Examination of three simulated borehole (SBH) samples revealed cracking along the contact of grout to anhydrite in the two samples that had leaked during permeability testing. No such openings were found in the sample that had not been tested. It is thought this cracking was due to such factors as drying, removal of outer restraint, and inadequate thickness of restraining anhydrite or combinations of these factors. Improved methods of fabricating such samples to simulate the actual contact of grout and host rock are still needed.

- f. Examination of grout from the upper and lower parts of satellite holes showed that sand from the bottom of the hole was carried up into the grout during placement and that brine already present in these holes caused areas of high water content incompetent grout in these samples.

It is not known how good a simulation these grout-filled holes are of the actual conditions in Hole AEC-7. It is possible that the grout in Plugs 1 and 2 is also most competent in the center and less so at the bottom and top portions of the plugs. If so, it may be that field permeability data for the Bell Canyon aquifer[4] were based on a smaller amount of competent grout acting to block this passage than has been believed since the upper and lower portions of each plug may have been disturbed like that in the satellite holes.

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3. Rhoderick, J. E. and Buck, A. D., Examinations of Simulated Borehole Specimens, U. S. Army Engineer Waterways Experiment Station, Miscellaneous Paper SL-81-7, May 1981, Vicksburg, Miss.

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Table 1

Results of Visual Inspection of Plugs 1 and 2 Grout Specimens at 13- Through 36-Months Age

Plug No.	Type of Sample	Age, months	Curing Environment	Type of Distress
1	3- by 3- by 10-in. restrained prism	18	Dry at 100° F	Cross cracking
1	3- by 3- by 10-in. unrestrained prism	18	Dry at 100° F	Cross cracking, single break in half along crack
1	2- by 2- by 10-in. restrained prism	18	Dry at 100° F	Cross cracking
1	2- by 2- by 10-in. unrestrained prism	18	Dry at 100° F	No visible cracking
1	1- by 1- by 10-in. prism	18	Dry at 100° F	Masked*
1	3- by 6-in. cylinders	18	Inundated in brine groundwater at 100° F	Some map cracking on top surface; some vertical and cross cracking; some spalling
1	NX cores from 6- by 12-in. cylinders	18	Inundated in brine groundwater at 100° F	No visible cracking
1	2- by 2- by 2-in. cubes	18	Inundated in brine groundwater at 100° F	Some cross cracking
1	15-in-long polyvinyl tubes	18	Inundated in brine groundwater at 100° F	Some map cracking, arch cracking

(Continued)

Table 1 (Continued)

Plug No.	Type of Sample	Age, months	Curing Environment	Type of Distress
1	Piece from 6- by 12-in. cylinder	24	Inundated in brine groundwater at 100° F	Some map cracking
1	Piece from 6- by 12-in. cylinder	36	Inundated in brine groundwater at 100° F	Some map cracking
2	3- by 3- by 10-in. restrained prism	13	Semiwet, in plastic bags, over brine groundwater at 100° F	Masked*
2	3- by 3- by 10-in. unrestrained prism	13	Semiwet, in plastic bags over brine groundwater at 100° F	Masked*
2	2- by 2- by 10-in. prism	13	Semiwet, in plastic bags over brine groundwater at 100° F	Masked*
2	3- by 3- by 10-in. restrained prism	13	Inundated in brine groundwater at 100° F	Longitudinal, cross, diagonal, and arch cracking; some samples were masked*, spalling
2	3- by 3- by 10-in. unrestrained prism	13	Inundated in brine groundwater at 100° F	Same cracking as restrained 3-in.; spalling
2	2- by 2- by 10-in. restrained prism	13	Inundated in brine groundwater at 100° F	Masked*
2	2- by 2- by 10-in. unrestrained prism	13	Inundated in brine groundwater at 100° F	Masked*
2	1- by 1- by 10-in. unrestrained prism	13	Inundated in brine groundwater at 100° F	Longitudinal, cross, diagonal cracking; less cracking than larger samples

(Continued)

Table 1 (Concluded)

Plug No.	Type of Sample	Age, months	Curing Environment	Type of Distress
2	3- by 6-in. cylinder	13	Inundated in brine groundwater at 100° F	Longitudinal, cross, cracking; sample broke in half along crack, concave/convex break
2	6- by 12-in. cylinder	13	Inundated in brine groundwater at 100° F	Some cross, horizontal, and arch cracking; spalling
2	2- by 2- by 2-in. cube	24	Inundated in brine groundwater at 100° F	Some cross and arch cracking
2	2- by 2- by 2-in. cube	36	Inundated in brine groundwater at 100° F	Some cross and arch cracking

* Surface covered with a spray-on plastic coating.

Table 2

Phase Composition of BCT-1-FF Grout in Plugs 1 and 2 by X-Ray Diffraction

	Ettringite	$C_4\bar{A}\bar{S}H_{12}$	Calcium Hydroxide	$C_3A(CaCl_2)H_{10}$	Calcium Silicate Hydrate	Unhydrated Cement	Quartz	Hydro-garnet	Gypsum
Plug 1 Cube Sample A4									
15 days old	X*	X	X	--	X	X	X	X	--
28 days old	X	X	X	--	X	X	X	X	--
56 days old	X	X	X	X	X	X	X	X	--
90 days old	X	X	X	X	X	X	X	X	--
180 days old	X	X	--	X	X	X	X	X	--
370 days old	X	Poss.**	--	X	X	X	X	X	X
2 years old	X	X	X	--	X	X	X	X	--
3 years old	X	Poss.	X	X	X	X	X	X	--
Plug 2 Cube Sample CL-30 GRT-158									
55 days old	X	--	X	X	X	X	X	--	--
90 days old	X	--	X	Poss.	X	X	X	--	--
180 days old	X	--	X	X	X	X	X	--	--
370 days old	X	--	X	X	X	X	X	--	--
2 years old	X	Poss.	X	X	X	X	X	X	--
3 years old	X	Poss.	X	X	X	X	X	Poss.	--
Portion of High-Strength NX Core									
About 15 Months	X	Poss.	X	--	X	X	X	Poss.	--

* An X indicates a phase is present.

** Possibly present.

Table 3

Chemical Analysis of 10 lb Brine CL-30 W-3

from Hole AEC-7*

Elements	Mg/ℓ	Other Data	
Al	<10	Alkilinity as $CaCO_3$	46
Ca	1600	Ph	6.8
Fe	46	% Solids	31.37
K	73	% Vol 550° C	2.02
Mg	85	% Vol 800° C	0.30
Mn	1		
Na	112,000		
Si	20		
Cl	143,400		
SO_4	10,000		

* 1 gal taken at time of Plug 2 placement; received for analysis on 9 December 1980.

Figure 1. Plug 2 unrestrained prism CL-30 GRT-6 that broke at approximately 1-year age. Note the cracking on the surface and the faint white crack in the center of the top surface, X0.25

Figure 2. Plug 2 cube CL-30 GRT-158 after it had been sawed to obtain a 370-day-old sample. Notice the white material on the outer surfaces of the cube, X0.38

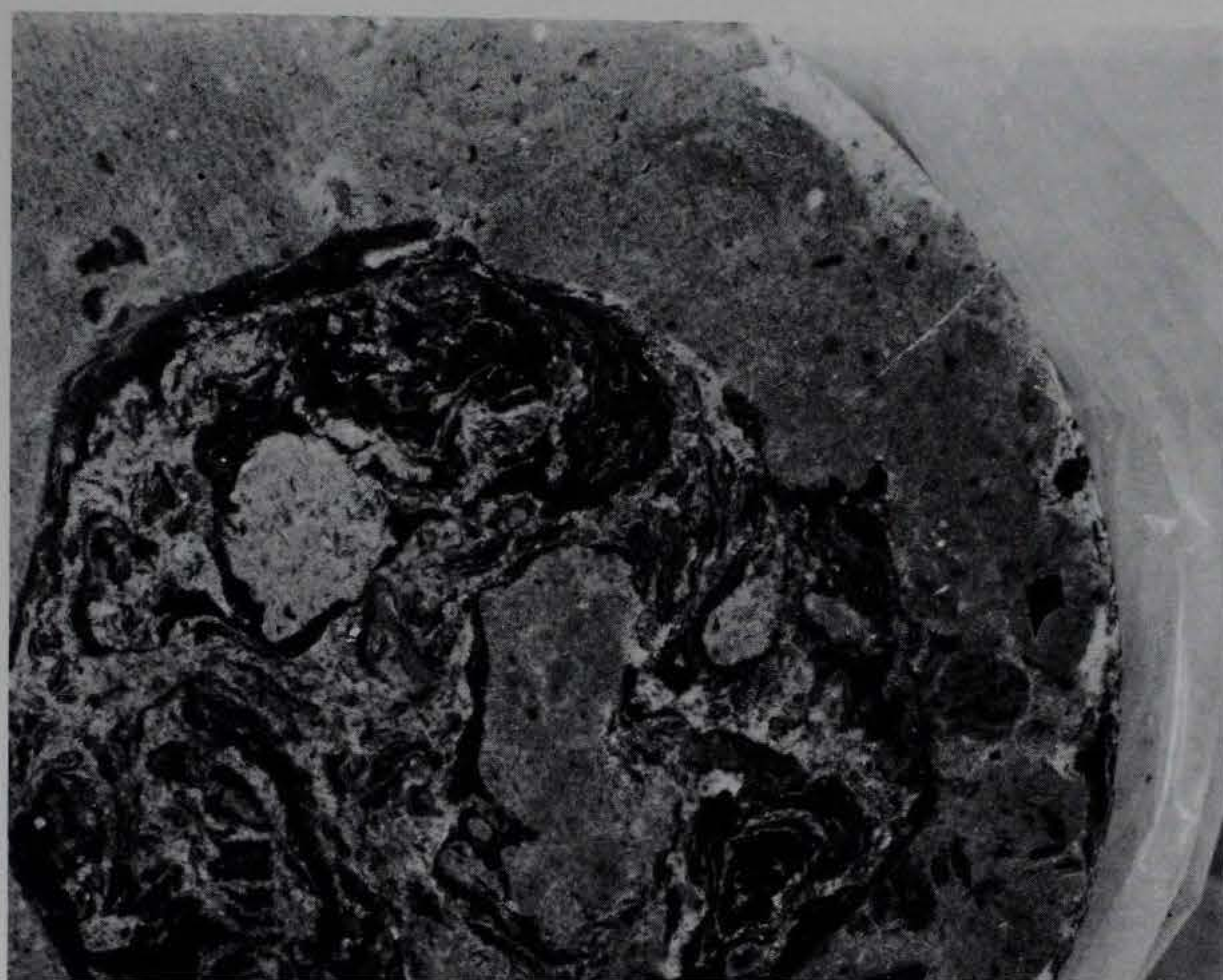

Figure 3. Bottom surface of sample A11 from top of satellite Hole 4. The middle of the hardened grout shows a mottled effect caused by the infiltration of brine into the mixture. The difference in coloration is probably due to areas of high (light colored areas) and lower (dark colored areas) water contents. About natural size

Figure 4. Sample A12 from bottom of satellite Hole 4. Note the sand particles in the center and some on the outer upper perimeter. The lower right corner shows the discoloration found in the sample; is probably carbonation. About natural size

Figure 5. Sample A12 from satellite Hole 4. The sand was mixed into most of it. Note the voids in the sample due to the turbulence during placement. The sample is 1.1 ft long

Figure 6. Micrograph 030581-11, X500. Typical morphology of Plug 1 cube A4 showing some fly ash spheres on a broken surface. The age is intended to be equivalent to 370 days

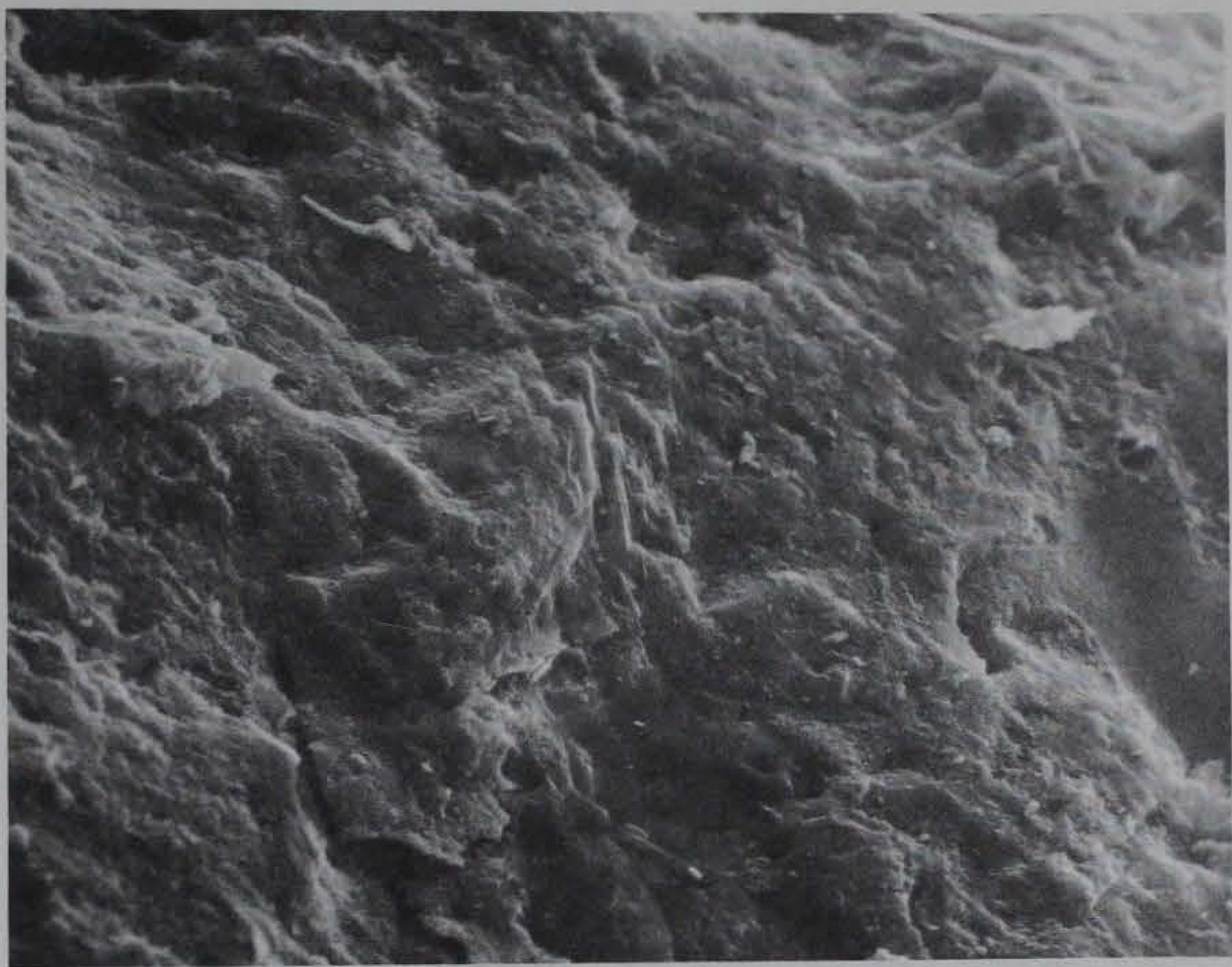

Figure 7. Micrograph 030581-36, X480. Typical morphology of Plug 2 cube CL-30 GRT-158. This broken surface at 370-days age equivalent appears denser than the Plug 1 samples seen in Figure 6

Figure 8. Micrograph 030581-26, X1900. Broken surface of Plug 2 cube CL-30 GRT-158. An unhydrated cement grain is seen in the upper left corner, bordered by calcium hydroxide and calcium silicate hydrate. The specimen was about 1 year old

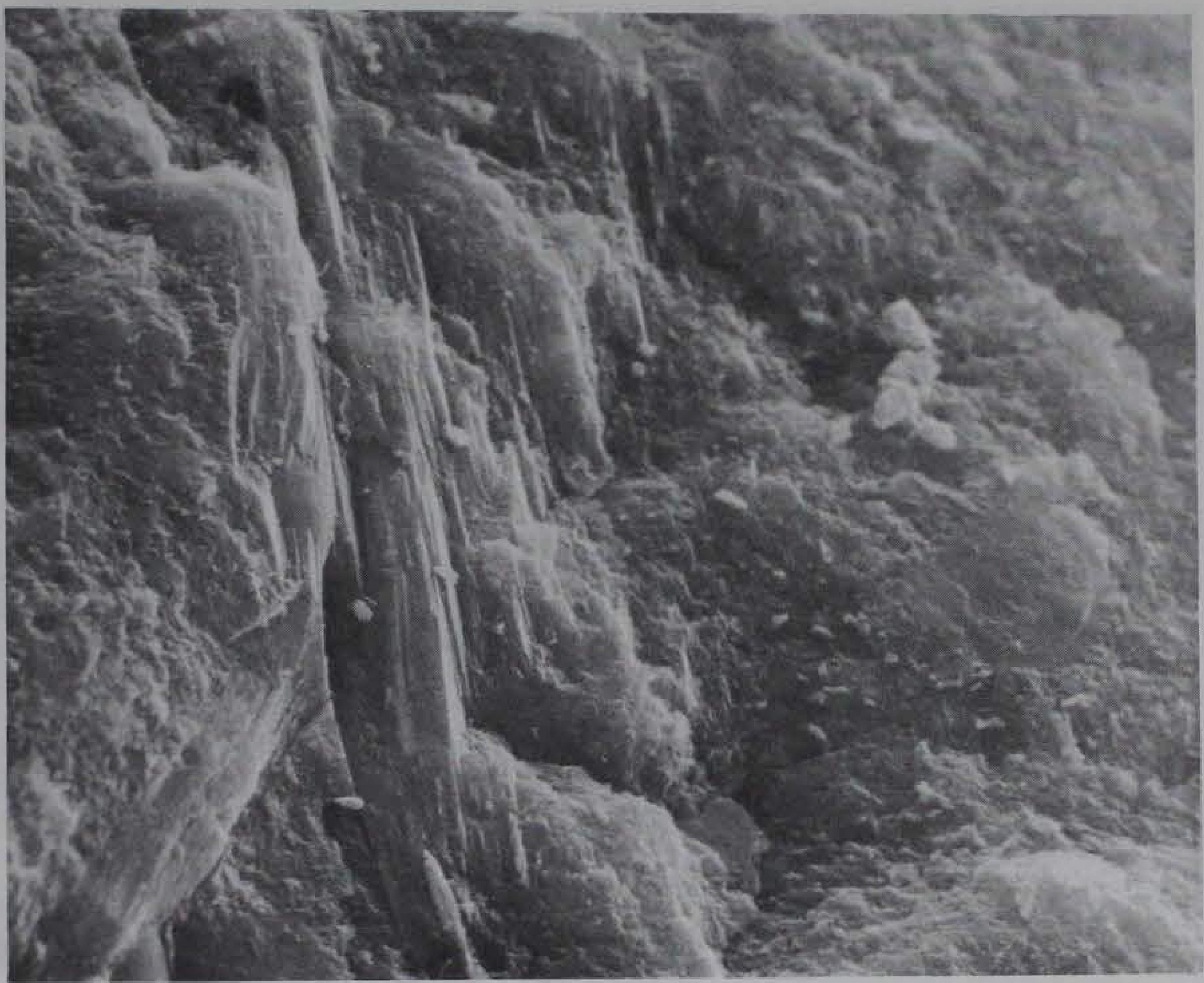

Figure 9. Micrograph 030581-34, X1900. Broken surface of Plug 2 cube CL-30 GRT-158. Massive calcium hydroxide crystals surrounded by calcium silicate hydrate. The sample was about 1 year old

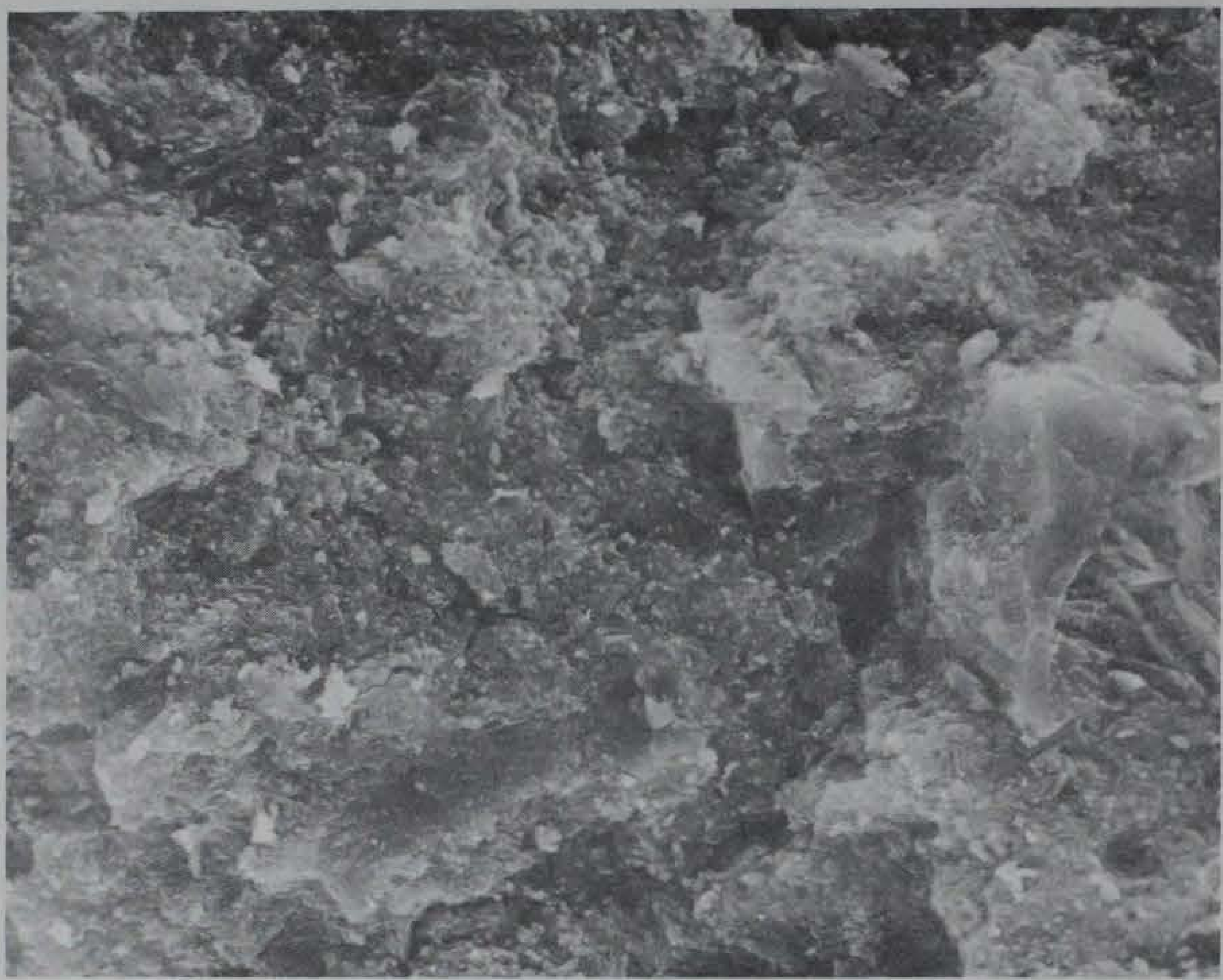

Figure 10. Micrograph 030581-10, X2000. Broken surface of Plug 1 cube A4. This surface shows more porosity than the Plug 2 cube surface (Figures 8, 9). The sample was about 18 months old

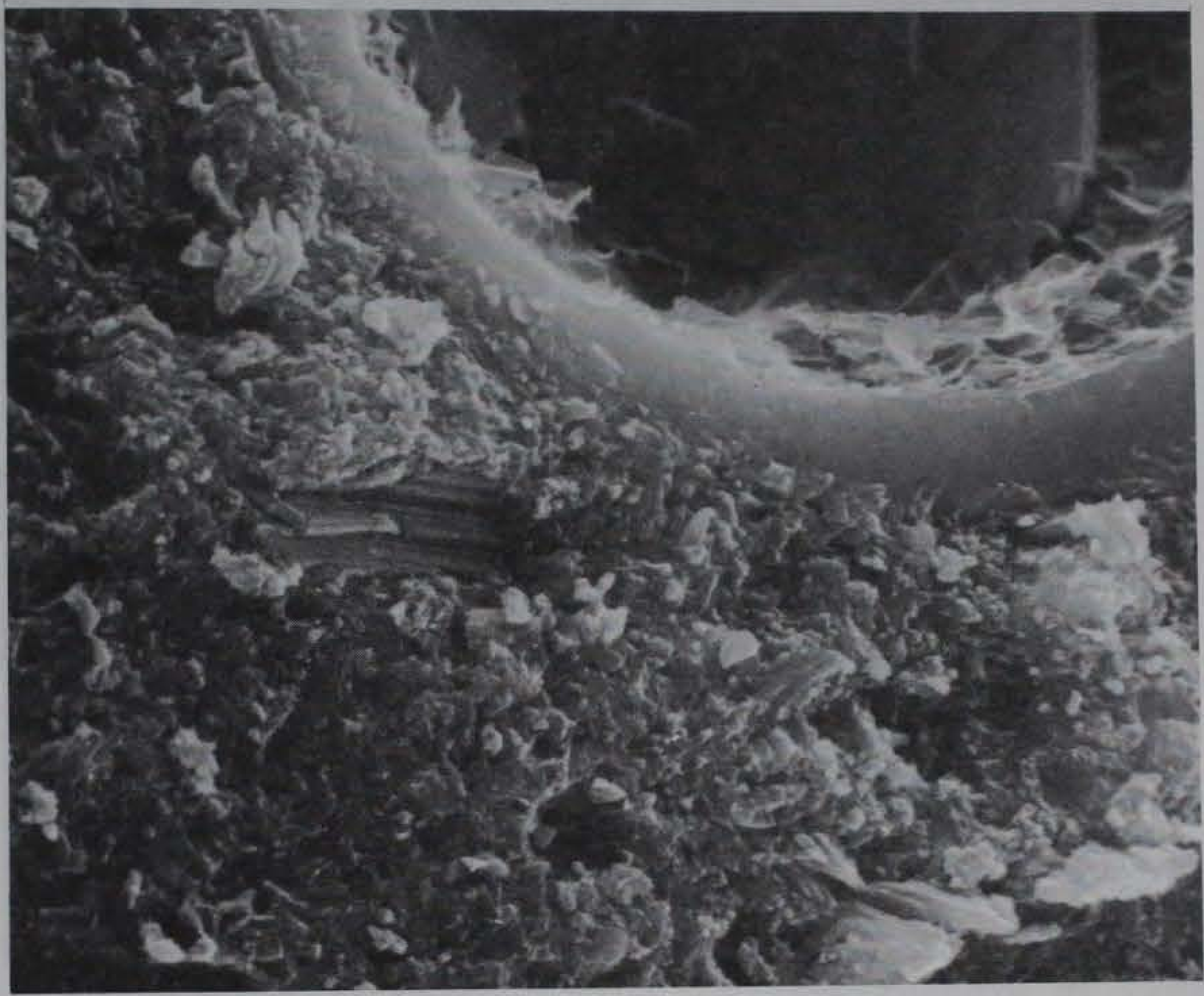

Figure 11. Micrograph 030581-6, X5000. Broken surface of Plug 1 cube A4. A broken fly ash sphere in upper right surrounded by calcium silicate hydrate and calcium hydroxide crystals. The sample was about 18 months old

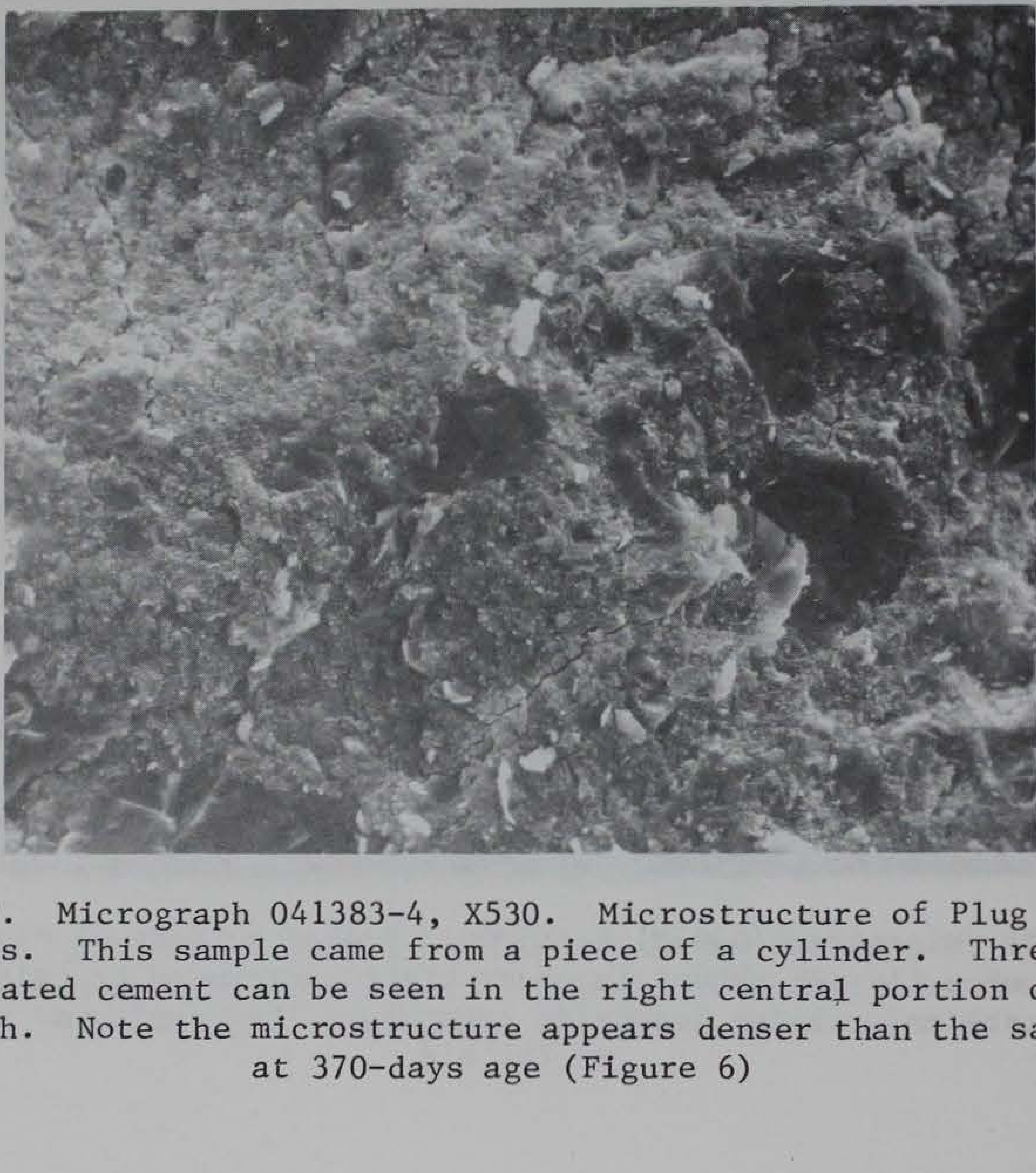

Figure 12. Micrograph 041383-4, X530. Microstructure of Plug 1 grout at 3 years. This sample came from a piece of a cylinder. Three grains of unhydrated cement can be seen in the right central portion of the micrograph. Note the microstructure appears denser than the same grout at 370-days age (Figure 6)

Figure 13. Micrograph 041383-15, X510. Microstructure of Plug 2 grout at 3 years. This sample came from cube CL-30 GRT-158 grout. The surface of this grout looks denser than Plug 1 grout of the same age (Figure 12). Unhydrated portland cement and fly ash spheres can be seen in the micrograph. A broken fly ash sphere is in the upper central portion of the micrograph

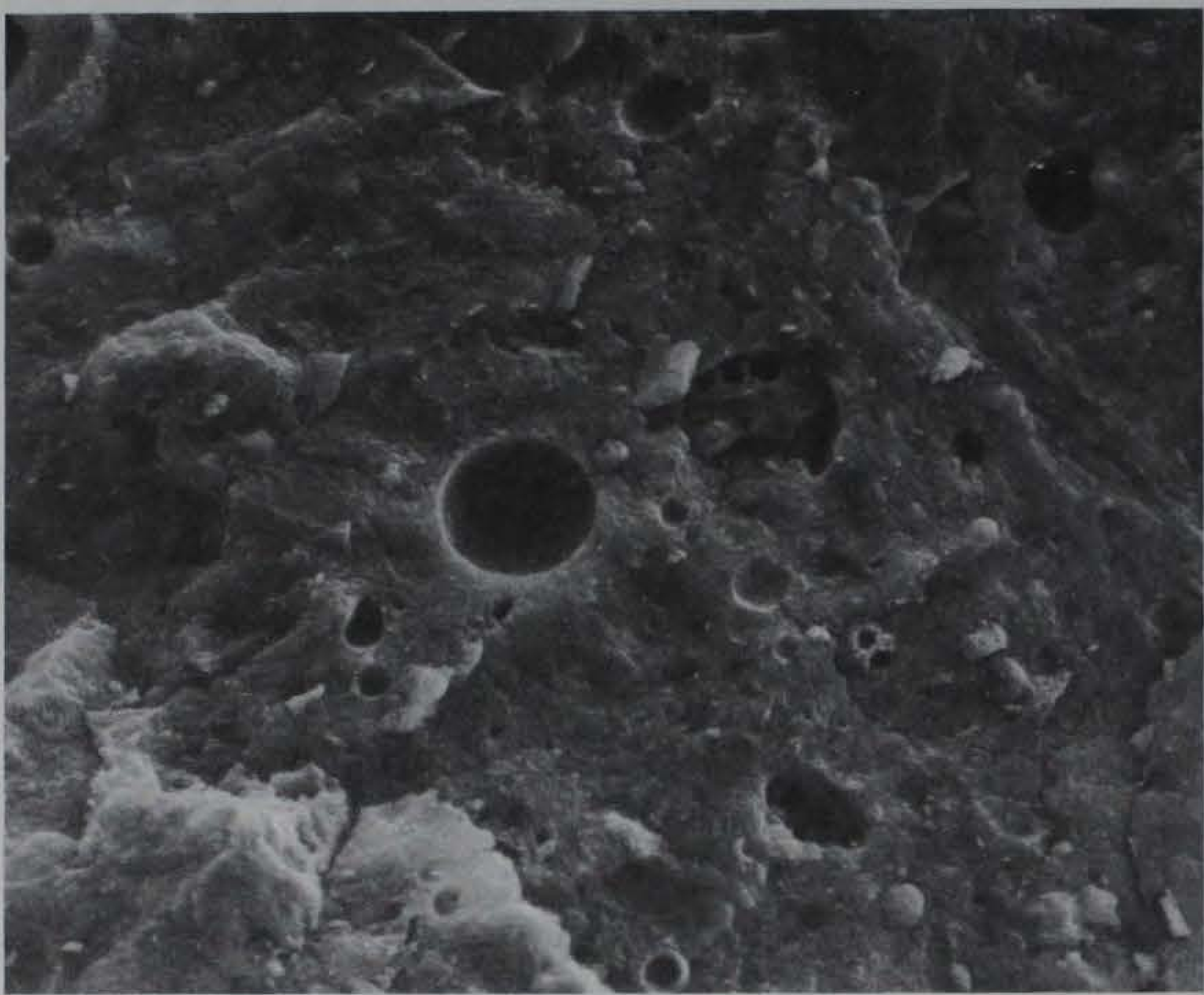

Figure 14. Micrograph 051381-18, X525. Plug 2 grout at 15-months age. This sample came from the high-strength (25,000+ psi) NX core. The fractured surface shows a dense microstructure. Several impressions of fly ash can be seen in the surface. The spheres pulled away with the other portion when the fracture was made