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EXAMINATION OF SAMPLES OF BELL CANYON TEST 1-FF GROUT.(U)
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EXAMINATION OF SAMPLES OF BELL CANYON TEST 1-FF GROUT

by

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Portland cement grout identified as BCT-1-FF (Bell Canyon Test 1-FF) was used in borehole plugging experiments of the Bell Canyon Tests in Hole AEC-7 at the Waste Isolation Pilot Plant site in New Mexico during September 1979 and February 1980. This grout was made with fresh water. A study of this grout was begun in August 1979 in the laboratory to evaluate the possible effects of temperature, pressure, and storage in fresh water or simulated groundwater (brine) on its phase composition and compressive strength at early ages.

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20. ABSTRACT (continued)

Phase composition was determined by X-ray diffraction. Temperatures ranged up to about 150°F and included elevation at a few hours age after mixing; pressure was as high as 1500 psi; specimens were stored in simulated groundwater (brine) or in fresh water.

Data from 1 to 90 days showed:

a. Higher temperature accelerated early strength gain. These differences essentially vanished by 90 days age.

b. Hydration products as identified by X-ray diffraction were normal; this indicated that a temperature range of 78 to 153°F was not significant.

c. Pressure did not affect composition.

d. Storage in simulated groundwater (brine) or fresh water had no detectable effect.

e. Since the BCT-1-FF grout mixture contained added sulfate, it formed more ettringite as judged by X-ray diffraction than comparable portland cement mixtures without added sulfate.

Preface

This work was begun with funds provided by Sandia National Laboratories, Albuquerque, N. Mex., in FY 1979. It was completed in FY 1981 under Department of Energy Contract No. DE-AI97-81ET46633. The work was part of the preparation for the Bell Canyon Tests at the Waste Isolation Pilot Plant site conducted by Sandia. Mr. C. W. Gulick, Jr., was Sandia Project Officer. Mr. Floyd L. Burns, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio, was Project Manager for the completion of the laboratory work.

The work was done in the Structures Laboratory of the U. S. Army Engineer Waterways Experiment Station (WES) under the direction of Mrs. Katharine Mather, Project Leader. Mr. Bryant Mather was Chief of the Structures Laboratory, and Mr. John M. Scanlon, Jr., was Chief of the Concrete Technology Division (CTD). The advice and assistance of Messrs. John A. Boa, Jr., and Donald M. Walley of the Grouting Unit, CTD, are gratefully acknowledged. This report was prepared by Messrs. Jay E. Rhoderick, Ging S. Wong, and Alan D. Buck.

Director of WES during the work was COL N. P. Conover, CE. Technical Director was Mr. F. R. Brown.

Contents

Conversion Factors, Inch-Pound to Metric (SI) Units of Measurement

Inch-pound 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 or Kelvins*
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 (U. S. liquid)	80.51963	kilograms per cubic metre

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* 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: $K = (5/9)(F - 32) + 273.15$.

EXAMINATION OF SAMPLES OF BELL CANYON TEST 1-FF GROUT

Background

1. During a planning meeting at the Waterways Experiment Station (WES) on 14 August 1979 (Gulick et al. 1980), it was decided that the grout to be used in the Bell Canyon field test would be made with fresh instead of salt water. The field tests were made during September 1979 and February 1980, at the Waste Isolation Pilot Plant (WIPP) site in New Mexico.

2. Small batches of this same freshwater grout were made on three different days in the laboratory, treated in different ways, and examined by X-ray diffraction at different ages to investigate the effects of the treatments on the grout at a series of relatively early ages.

3. This work was the first experimental work for the Geochemical Program by the WES Structures Laboratory (SL) for the Office of Nuclear Waste Isolation (ONWI). The work was done in the last 2 months of FY 79 and the first few months of FY 80.

Test Procedure

4. The grout for Conditions 1 through 4 was made on three dates and cast in glass vials 7/8 in.* in diameter and 2-3/8 in. long. The vials were all stored in laboratory-made simulated brine groundwater at several temperatures and pressures. The grouts were examined by X-ray diffraction at ages from 7 to 90 days.

5. The grout for Conditions 5 and 6 was made in 1 day and cast in glass vials and cube molds 2 by 2 by 2 in. All of the specimens were subjected to accelerated curing in fresh water at constant or varied temperatures. Specimens from the vials were examined by X-ray diffraction, and cubes were broken at 1-, 2-, 3-, 7-, 14-, and 90-day ages. Embedded and external thermocouples were used to monitor the specimen temperature

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

for Conditions 5 and 6. Temperature measurements for the other conditions were based on external measurements.

6. X-ray samples were prepared by breaking the glass vials and removing the broken glass. The grout specimens were then sawed along their long axis. Specimens from Conditions 1 through 4 were sawed dry or using water as a coolant. Specimens from Conditions 5 and 6 were sawed using water as a coolant. Each specimen was cut to be a 1-in. length, and a sawed surface of each was ground smooth using methanol as a lubricant. The prepared surfaces were then placed in a closed nitrogen (N_2) environment to prevent carbonation of the grout. A beaker of hot barium hydroxide or a sponge soaked in it was then added, and each specimen was examined by X-ray diffraction. The liquid is added in the closed environment to raise the relative humidity so that hydration products will not dehydrate. All X-ray patterns were made with an X-ray diffractometer, using nickel-filtered copper radiation.

Results

7. The composition of the simulated brine is shown in Table 1.

8. Table 2 shows when specimens were made, environmental conditions, and when they were examined by X-ray diffraction. Conditions 1 through 4 represented storage in brine and some pressure as well as temperature differences. Conditions 5 and 6 represented differences in accelerated curing temperature.

9. The temperature of the Condition 5 and 6 grout was monitored. The results for the first 28 hours are shown in Figure 1. After 28 hours, the higher temperature was reduced to match the lower one, and they stayed approximately equal until testing was completed. The two temperatures equalized after about 48 hours. The differences in temperatures had the expected effect on strength development. Table 3 shows the compressive strength data. Condition 5 strengths at the lower constant temperature were significantly lower for the first 7 days. After that, strengths were similar for the two conditions. This was as expected.

10. The composition of BCT-1-FF grout is shown in Table 4.

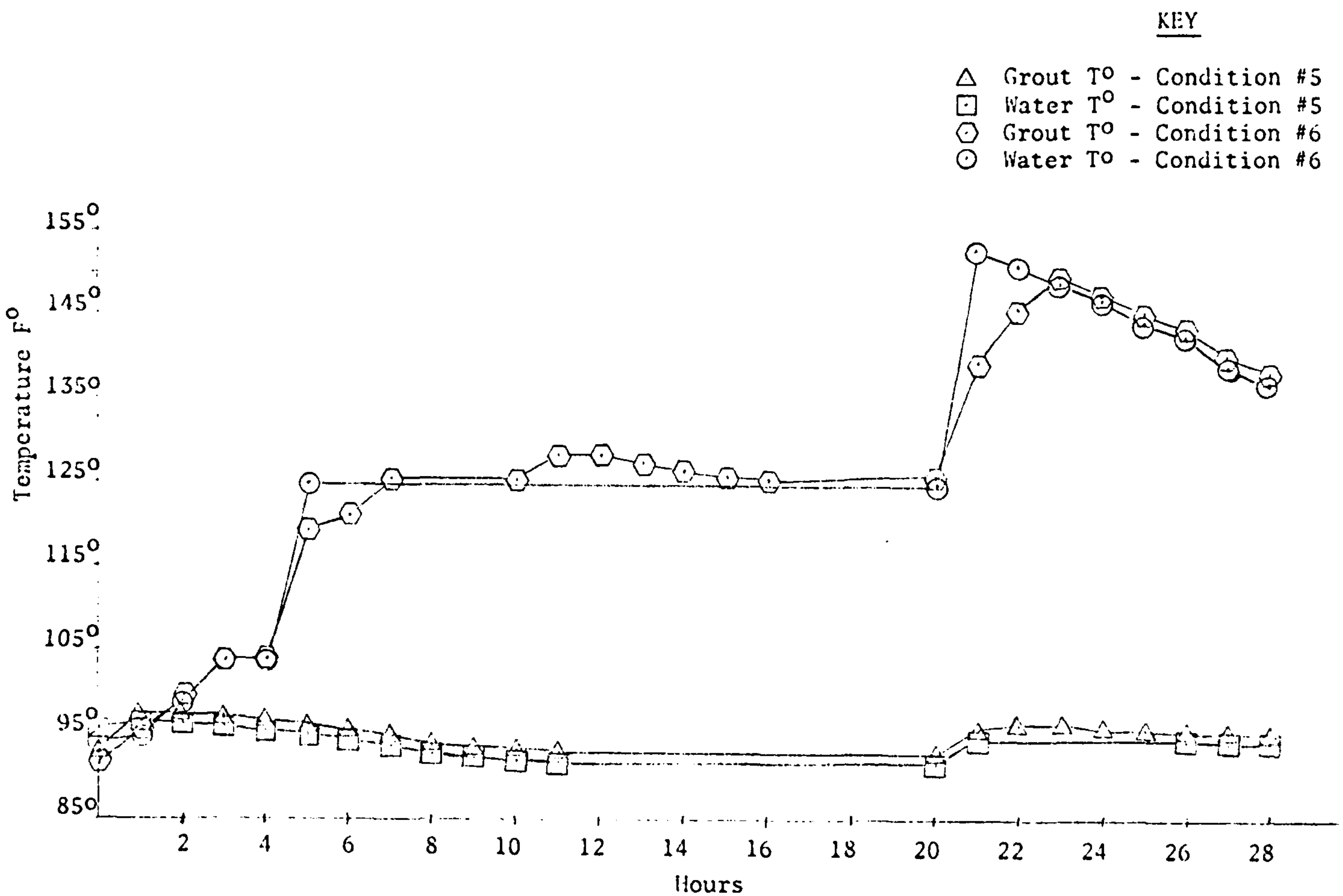

Figure 1. Time-temperature records for Conditions 5 and 6

11. Consideration of the information presented in Table 4 might lead to an expectation of identifying unhydrated portland cement, fly ash, hydrated calcium sulfate, and cement hydration products in X-ray diffraction patterns of this grout. There was also a possibility that tetracalcium aluminate dichloride-10-hydrate (chloroaluminate) might be present for those specimens stored in brine. The Condition 2 vial was stored in the brine without a stopper, and several vials had cracked during storage. However, aside from the possible presence of a little chloroaluminate in the Condition 4 sample at 7 days, this material was absent from the grout samples. It might have been present on the outer surface of some samples, but the X-ray diffraction examination was always made on the interior surfaces.

12. While the early age temperature difference in Conditions 5 and 6 had a significant effect on strength, the effects of temperature or pressure were not as readily apparent in the X-ray diffraction patterns. The usual composition determined by X-ray diffraction was unhydrated cement, fly ash as quartz, and the cement hydration compounds ettringite and calcium hydroxide (Table 5). A small amount of the cement hydration compound tetracalcium aluminate monosulfate-12-hydrate (monosulfoaluminate) may have been present in many of the X-ray patterns.

13. Specific comments about the samples follow:

<u>a</u>. The 1-day-old Condition 5 sample contained some gypsum ($CaSO_4 \cdot 2H_2O$) which decreased at 2 days and was missing thereafter. This represented some of the RC-626 which had not all been used in the first 2 days. There was no gypsum in the early age Condition 6 samples, and none of the other conditions were examined at such an early age so it was not found in them. The accelerated temperature of Condition 6 was in effect within 3 hours after the grout was mixed and put into the accelerated tanks. This greatly increased hydration as evidenced by a compressive strength of 7420 psi for the higher temperature and only 3020 psi for the lower temperature at 1 day (Table 3). The difference in rate of hydration explains why gypsum was present in the Condition 5 samples at 1 and 2 days; hydration had not progressed far enough to use up all of the RC-626. The other evidence of difference in the early age Condition 5 and 6 samples by X-ray diffraction was that the 2.97-Å (0.30-nm) peak of alite was stronger,

indicating less hydration, in the lower temperature Condition 5 sample.

b. Small amounts of monosulfoaluminate were probably present in most samples after the 1-day age, but none was found in the 1-day-old Condition 5 sample or the 1- and 2-day-old Condition 6 samples. Other conditions were not examined at such early ages. Its presence was considered normal.

c. Since calcium silicate hydrate (CSH) is poorly crystaline, its presence may not be recognizable in X-ray diffraction patterns of hydrated cement paste. It was present in all patterns although it was not specifically recognized by peaks.

Conclusions

14. Compressive strength data and examination of hydrated grout samples by X-ray diffraction at ages ranging from 1 to 90 days indicated:

a. The higher early age temperatures of about 153°F resulted in significantly higher strengths for the Condition 6 specimens for the first 7 days, after which time the strengths were similar. This difference was less apparent by X-ray diffraction. It could be detected by the presence of unused RC-626 and more alite in the Condition 5 samples at an early age.

b. In general, the hydration products were the expected ones; the faster rate of hydration with higher temperatures did not affect the composition. A limited amount of other X-ray diffraction work (WES 1980) on a saltwater grout mixture (BCT-1-FF) at ages up to 79 days and temperatures ranging from 78 to 128°F indicated that hydration was normal for the materials involved. These early age hydration products were found to be similar to saltwater grouts that were up to 17 years old (Buck and Burkes 1979). Thus, it can be said that hydration of grout mixtures appears normal in composition for temperatures ranging from 78 to 153°F. Higher temperature effects have not been investigated at this time.

c. The differences in pressure among the Condition 1 through 4 samples did not result in detectable differences by X-ray diffraction.

d. There was no effect of storing in brine on the Condition 1 through 4 samples that were examined. It is likely that some chloroaluminate did form on the surface of the Condition 2 vial that was not capped and on grout surfaces of vials that cracked during storage. Other work* has shown that conversion of ettringite to chloroaluminate when freshwater grout smaples are exposed to brine is limited to the outer 1/4 in. for ages up to 90 days. Later age samples were not examined.

e. Comparison by peak height of ettringite in X-ray patterns of the present samples with X-ray patterns of other portland cement paste mixtures (Mather et al. 1978) indicates more ettringite in the present samples. This is due to the addition of the RC-626 to the BCT-1-FF mixture making additional sulfate available to form ettringite.

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* U. S. Army Engineer Waterways Experiment Station. "Examination of Simulated Borehole Specimens," unpublished results, Vicksburg, Miss.

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Table 1

Composition of Laboratory Simulated Brine Groundwater*

Ion	Composition, mg/l	
	Calculated	Analyzed
Cl	181, 700	180, 400
Na	122, 422	--
SO_4	12, 110	12, 700
Mg	675	494
pH	--	6.3-7.0

* From Boa (1978).

Table 2

Descriptive Data for BCT-1-FF Grout Sample

Test Conditions	Age When Specimens Examined By X-ray Diffraction, Days							
	1	2	3	7	14	16	19	90
Condition 1 - Cast in 2 vials on 17 August 1979. Stored at 100°F in brine							X	X
Condition 2 - Cast in 2 vials on 21 August 1979. Temperature varied from 92 to 150°F, stored in brine without sealing. Kept at 1500 psi				X				
Condition 3 - Cast in 2 vials on 21 August 1979. Temperature varied between 92 and 142°F. Stored in brine						X		X
Condition 4 - Cast in 2 vials on 23 August 1979. Stored in brine at 100°F and 1500 psi								X
Condition 5 - Cast in 6 vials and 6 cubes (2 by 2 by 2 in.) on 21 August 1979. Stored in fresh water at 92 to 97°F	X	X	X	X	X			X
Condition 6 - Cast in 6 vials and 6 cubes (2 by 2 by 2 in.) on 21 August 1979. Stored in fresh water at 92 to 153°F	X	X	X	X	X			X

Table 3

Compressive Strength of BCT-1-FF Grout Cubes At Constant or Varied Temperature

Age, Days	Compressive Strength, psi*	
	Condition 5, Constant Temperature**	Condition 6, Variable Temperature†
1	3,020	7,420
2	6,120	10,660
3	7,540	10,720
7	10,350	13,980
14	11,380	13,620
90	15,000	over 15,100

* Each value is for one 2- by 2- by 2-in. cube tested in accordance with CRD-C 227-78.

** Ranged from 92 to 97°F.

† Ranged from 92 to 153°F.

Table 4

Batch Data for Grout

Mixture BCT-1-FF

Cement, Class H, lb/cu ft	66.6
RC-626, lb/cu ft	8.9
Fly ash, lb/cu ft	22.4
Water-reducing admixture, lb/cu ft	0.28
Water, lb/cu ft	29.4
Water-solids ratio	0.299
Density, lb/gal	17.05

Table 5

Composition* of Condition 5 and 6 Grout at Four Ages

Constituent	Composition at Cited Age, days 1	3	14	90
Condition 5 (92 to 97°F) Grout				
Portland cement				
Unhydrated	X[**] (1)[†]	X	X	X (2)
Hydrated				
Ettringite	X (2)	X	X	X (1)
Calcium hydroxide	X	X	X	X
Monosulfoaluminate[††]	n.d.[#]	n.d.	n.d.	Probable
Quartz (fly ash)	X	X	X	X
Gypsum (from RC-626)	X (1)	n.d.	n.d.	n.d.
Condition 6 (92 to 153°F) Grout				
Portland cement				
Unhydrated	X (1)	X	X	X (2)
Hydrated				
Ettringite	X (2)	X	X	X (1)
Calcium hydroxide	X (1)	X (1)	X (1)	X (2)
Monosulfoaluminate	n.d.	n.d.	n.d.	Probable
Quartz (fly ash)	X	X	X	X
Gypsum (from RC-626)	n.d.	n.d.	n.d.	n.d.

* As indicated by X-ray diffraction.

** Indicates a phase present.

† Indicates relative amount of a compound; (1) is more, (2) is less.

†† Tetracalcium aluminate monosulfate-12-hydrate.

# Indicates not detected.

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