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Bell Canyon Test (BCT) Cement Grout Development Report

Charles W. Gulick, Jr., John A. Boa, Jr., Alan D. Buck

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Additional supporting laboratory studies were performed by the Dowell Regional Laboratory at Midland, Texas, by Dr. D. M. Roy and her co-workers at the Materials Research Laboratory of Pennsylvania State University, and J. G. Moore and his co-workers at the Oak Ridge National Laboratory. These data and published results are included in "Laboratory Development at Dowell, PSU, and ORNL" of this report.

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BELL CANYON TEST (BCT) CEMENT GROUT
Development Report

Introduction

Cementing materials development studies for the Borehole Plugging Program (BHP) have been underway at the U.S. Army Engineer Waterways Experiment Station (WES) Structures Laboratory (formerly Concrete Laboratory) since 1975. The study is sponsored by the Waste Management Technology Department of Sandia National Laboratories, which has technical responsibility for supporting development of the Waste Isolation Pilot Plant (WIPP) in southeastern New Mexico.

Purposes of the BHP cement program are:^{1,2}

1. To develop materials and techniques for plugging boreholes through and adjacent to underground waste disposal facilities.
2. To seal boreholes with plugs that will prevent fluids and gases from moving toward or through the salt beds.
3. To develop plugs that will maintain their integrity for periods comparable to the life of the rock formations in which they are emplaced.

Several review meetings have concluded that the only material and technique currently available for plugging boreholes is high quality cementing.^{1,3} These conclusions were the impetus and are the basis for the long-range development and testing program at WES. Two continuing tasks of the Materials Development Program have been to:

1. Combine an extensive laboratory program with field supervision and quality control of grouting operations.

2. Continue study of representative field samples prepared at the surface and, when possible, cores of downhole plugs.

Some of the desirable properties that plugging grouts should have are low permeability, low porosity, high density, high strength, expansive potential, isotropy, homogeneity, pumpability, adequate working time, stability, and durability. The effect of water-cement ratio on the quality of portland cement products has long been recognized. Pumpable grouts generally require far more water than is necessary for complete hydration of the cement. Reduction in water-cement ratio has been studied and achieved by various combinations of the following: Coarseness of the grind of the cement, water reducers (including high range water reducers, or "superplasticizers," and turbulence-inducing compound), retarders, and temperature of the grout slurry. Lowering the water-cement ratio generally reduces the permeability and porosity and increases the density and strength.

Expansive-cement systems have been included to provide a positive expanding force against the rock surface of the borehole after it hardens. This force should reduce the number of microfractures in the distressed annulus of rock around a plug for a tighter interface contact between the plug and the rock. Improved bonding should resist plug movement and improve impermeability of the plug, particularly at the interface. Two expansive-cement systems have been used, Type K expansive cement and the DOWELL* self-stress cement.

Both fly ash and natural pozzolans have been included in the studies to determine their effects on porosity, permeability, and durability. Fly ash has been included in all mixtures (30% by solid volume replacement for cement) to reduce early age temperature rise and to contribute to later age strength and durability by combining with calcium hydroxide to form the more stable and durable calcium silicate hydrates.

*Trademark of The Dow Chemical Company

Salt (sodium chloride) has been included in some grout mixtures because of the evaporite rock sections at the WIPP site. Brine prevents the salt rock at the interface from dissolving while free water is present in the grout.

Cements low in tricalcium aluminate (C_3A) are generally used in the Southwest and have been the basis of the grout mixtures. Low C_3A content is a major factor in resisting sulfate attack. Fly ash is also a factor in improving resistance to sulfate attack. The use of the lowest possible water-cement ratio and its effect on gel-pore structure of grout also has a significant effect on improving stability and durability of grout plugs.

Results of studies have been published.^{1 4 5} More comprehensive and detailed studies of cement hydration phases and interactions with wall rocks of boreholes are being carried out under the geochemical program at Sandia, WES, and Pennsylvania State University.

Laboratory Development Work at WES

The first review and planning meeting for the Bell Canyon Test (BCT) was held in January 1979. Three basic grout mixtures were proposed for simultaneous testing and screening for later selection as the field mixture. Data for the three mixture proportions are listed in Table 1.

The proposed mixtures were based on the materials development work at the U.S. Army Corps of Engineer WES Structures Laboratory at Vicksburg, Mississippi.^{1 2 3} Two of the mixtures used the relatively coarse grind Class H cement from the Lone Star Plant at Maryneal, Texas. Mixture DHT 3 used Class C (HSR) cement with a zero C_3A content (for sulfate resistance) from the same plant. Mixture DHT 1 included the DOWELL* Self-Stress Cement system for expansivity. All of the mixtures included 30% fly ash replacement

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TABLE 1
Proposed Basic Grout Mixtures

<u>Proportions (wt%)</u>	<u>DHT 1</u>	<u>DHT 2</u>	<u>DHT 3</u>
Class H Cement	48.7	53.0	--
Class C Cement	--	--	48.9
Expansive Additive	5.1	--	--
Fly Ash	17.1	17.9	16.9
Salt (NaCl)	7.7	7.7	7.6
Salt Gel	--	--	1.4
Water	21.4	21.4	25.2

(by volume) and salt brine mixing water. Salt brine was used in the development mixtures because of the unknown conditions of the surface of the wall rock at the plug location. Previous testing had indicated the desirability of including salt in the mixing water for plugs at locations where salt was the host rock and brine drilling mud had been used. The intention was to use the expansive DHT 1 mixture for the BCT (with adjustments and additives to achieve proper viscosity and maximum density), if the laboratory development testing showed suitable properties.

By the end of February 1979, 24 candidate grout mixtures had been formulated from these materials and tested for time of efflux, workability, density, and unconfined compressive strength (under accelerated curing at 128°F). Data for these studies are listed in Table 2. Criteria for pumpability required a flow of 18 seconds or less (through a flow cone) at the end of 3 hours. Intermittent mixing of 3 minutes during each 15-minute interval was done to simulate field conditions. An elevated temperature of 128°F was chosen for curing the specimens, both to accelerate the rate of strength gain and to match the expected downhole temperature for the BCT plug. During the plugging of ERDA 10 exploratory drill hole, downhole temperature at about the 4000-foot depth was reported to be 128°F.⁵

TABLE 2

Laboratory Grout Mixture Development Data

Designation	Mixture Components			Flow (sec)		Hardened	Unconfined
	w-c	Salt	Water Reducing Admixture, Type and Amount	Initial	3 hr	Density	Compressive Strength, 7 day
	Ratio	(%)	(lb/ft ³)			(lb/ft ³)	(psi)
<u>DHT 1 Series</u>							
(1)	.36	30		12.0	12.3	104.0 ^a	4465
(1) (A)	.36	30		9.8	11.5	111.5 ^a	4460
(2)	.30	36		13.6	20.7	102.8 ^a	3400
(2) (A)	.30	30		12.8	18.3	105.9 ^a	3745
(3)	.30	36	D-45, 0.1	13.9	21.5	104.4 ^a	2690
(3) (A)	.30	30	D-45, 0.1	13.7	17.2	b	
(4)	.30	36	D-45, 0.2	14.0	22.1	b	
(4) (A)	.30	30	D-45, 0.2	13.5	17.1	b	
(5)	.30	30	Melment, 3.0	11.5	11.4	b	
(6)	.26	30	Melment, 3.0	14.5	15.2	b	
(7)	.30	30	D-45, 0.2	13.2	20.1	b	
(8)	.30	30	D-65, 0.2	12.4	16.6	105.9 ^a	3790
(9)	.26	30	Melment, 1.5	15.8	16.2	128.3	6920
(10)	.33	30		10.5	12.9	108.4 ^a	4510
<u>DHT 2 Series</u>							
(1)	.36	30		10.8	11.1	127.7	6295
(2)	.30	30	D-45, 0.1	17.2	19.4	134.6	5085
(2) (A)	.32	30		14.3	15.6	132.7	9815
<u>DHT 3 Series</u>							
(1)	.40	29	Melment, 3.0	10.6	11.3	122.7	6600

TABLE 2--Continued

Designation	Mixture Components			Flow (sec)		Hardened	Unconfined
	w-c Ratio	Salt (%)	Water Reducing Admixture, Type and Amount (lb/ft ³)	Initial	3 hr	Density (lb/ft ³)	Compressive Strength, 7 day (psi)
(2)	.30	38	Melment, 3.0	15.5	18.5	b	
(3)	.30	30	Melment, 3.0	14.3	20.8	127.1	9565
(4)	.34	30	Melment, 3.0	13.5	13.8	124.6	10500
(5)	.32	30	Melment, 1.5	16.6	20.0	125.2	
(6)	.40	30		12.5	12.9	122.7	8125
(7)	.40	30	(Salt Gel Deleted)	10.5	12.3	123.4	7940

NOTES:

- General:
1. w/c ratio--Weight water divided by weight of cementitious materials (cement, fly ash, expansive additive).
 2. % Salt--Percent of NaCl by weight of mixing water.
 3. Flow (time of efflux), flow-cone method, CRD-6 79-58, Reference 4. After initial mixing, the grout mixture was mixed for 3 minutes out of each 15-minute interval for the 3-hour time period.
 4. Unconfined Compressive Strength was determined on 2-inch cubes cured in double plastic bags at 128°F.
 5. D-45--DOWELL turbulent flow additive for saturated salt water cements.
 6. D-45--DOWELL turbulent flow additive for cement.
 7. Melment--A high-range, water-reducing admixture Melment L-10A from American Admixtures.

^aLow density because of entrapped air during mixing--lack of defoaming agent.

^bSpecimens did not harden in 3 days' time.

Hardened density data for the DHT 1 series were lower than expected for all except DHT 1 (9) because of air entrapment during mixing for these high-density and low water-cementitious material ratio slurries. Subsequent work showed that a small amount of defoaming agent added to the mixing water reduced the excessive air entrapment for these high-density slurries.

The DHT 1 (9) expansive mixture was selected as having the optimum combination of properties for further development studies. Flow at the end of 3 hours was 16.2 seconds (compared with 7.6 seconds for tap water). Hardened density was 128.3 lb/ft³. Compressive strength values were 3470, 6920, and 8375 psi at 3, 7, and 14 days, respectively. All unconfined compressive strength tests were on 2-inch cubes cured inside double plastic bags at 128°F. Mixture proportions for DHT 1 (9) listed in percent by weight are given in Table 3. Expansive additive was 10.5% of the weight of Class H cement. The low water-cementitious material ratio of 0.26 gave a high fluid density of about 17.2 lb/gal and hardened density of 128.3 lb/ft³.

TABLE 3

WES Salt Grout Mixture

<u>Proportions (wt%)</u>	<u>DHT 1 (9)</u>
Class H Cement	50.6
Expansive Additive	5.3
Fly Ash	17.8
Salt (NaCl)	5.8
High-Range Water Reducer	1.3
Defoamer	0.02
Water	19.2
 <u>Properties</u>	
Water-Cementitious Ratio, by wt	0.26
Fluid Density (lb/gal)	17.2

Emphasis then shifted to determine expansion and bond strength properties of DHT 1 (9) mixture under various environmental conditions. Restrained expansion prisms conforming to ASTM C 806-75 were cured in different environments. Prisms were 3 x 3 x 10-in. with a 3/16-inch threaded steel rod providing restraint to the steel end plates. Data for the grout mixture with various modifications of additives and curing conditions are presented in Table 4. The two mixtures in Series 1 with fresh mixing water instead of brine had significantly higher expansions at 56 days. All Series 1 mixtures had positive expansion for inundated and elevated temperatures. Length reduction or negative expansion of Series 2 prisms shows the effect of drying shrinkage of the prisms through the flexible film of plastic and double plastic bags. Inundation of all prisms with brine mixing water was in saturated saltwater at the indicated temperature. Prisms with tap water mixing water were inundated in freshwater (no salt).

Tests of mechanical bonding of grout to rock were begun April 2. Samples cast as Simulated Borehole Specimens (SBS) were cast for pushout tests. Figure 1 is a cross-section of the SBS specimen showing the cored 2.25-inch hole along axis of a piece of 4-inch diameter anhydrite core from the AEC 7 or other exploratory drill holes at the WIPP site. The rock was grouted inside a 6-inch-diameter steel ring to provide restraint and to simulate horizontal confinement underground. Figure 2 shows the appearance of an SBS sample. Excellent resistance to movement of the center cylinder plug of grout was shown by a Bell Canyon sandstone sample--953 psi (Table 4). Bond strengths for the lower and upper anhydrite zones of 274 and 375 psi, respectively, were also considered adequate.

Using the mixture proportions developed by WES, the Dowell Division of the Dow Chemical Company adjusted the mixture by substituting a powder dispersant instead of the liquid high-range water reducer. Mixture proportions for this mixture (designated BCT-1F) are shown in Table 5. The expansive additive was also raised to 13% by weight of cement (10% by weight of cement plus fly ash). The water-cementitious ratio (including cement, fly ash, and expansive additive) was similar to DHT 1 (9) and the slightly lower fluid density of 17.0 lb/gal was considered acceptable. Physical property

TABLE 4

Restrained Expansion

Mixture DHT 1 (9), Series 1

<u>Expansion (%)</u>	<u>Age (days)</u>	<u>Remarks</u>
0.054	56	128°F, inundated
0.088	56	128°F, inundated without Melment
0.072	56	128°F, inundated with additional Melment
0.043	56	128°F, inundated with D-65 and defoamer
0.038	56	128°F, inundated with defoamer
0.036	56	128°F, inundated with D-65
0.027	56	128°F, inundated with added "A"
0.121	56	128°F, inundated freshwater (no salt)
30.094	56	128°F, inundated freshwater (no salt), without Melment

Mixture DHT 1 (9), Series 2

<u>Expansion (%)</u>	<u>Age (days)</u>	<u>Remarks</u>
.020	28	Ambient, coated, bagged, not inundated
-.002	56	Ambient, coated, bagged, not inundated
-.022	28	Ambient, coated, bagged, not inundated, without Melment
-.049	56	Ambient, coated, bagged, not inundated, without Melment

TABLE 4--Continued

Mixture DHT 1 (9), Series 2--Continued

<u>Expansion (%)</u>	<u>Age (days)</u>	<u>Remarks</u>
-.050	28	128°F, coated, bagged, not inundated
-.111	56	128°F, coated, bagged, not inundated
-.042	28	128°F, coated, bagged, not inundated, without Melment
-.027	56	128°F, coated, bagged, not inundated, without Melment

Mixture DHT 1 (9), Series 3

<u>Expansion (%)</u>	<u>Age (days)</u>	<u>Remarks</u>
.010	28	128°F, inundated
.042	56	128°F, inundated
.054	101	128°F, inundated
.018	28	Ambient, inundated
.020	56	Ambient, inundated
.056	104	Ambient, inundated

Mixture DHT 1 (9), Series 4

<u>Expansion (%)</u>	<u>Age (days)</u>	<u>Remarks</u>
.110	41	128°F, inundated, freshwater
.119	41	128°F, inundated
.055	41	128°F, inundated

TABLE 4--Continued

Miscellaneous [Variations of DHT 1 (9)]

<u>Expansion (%)</u>	<u>Age (days)</u>	<u>Remarks</u>
.083	28	128°F, inundated without fly ash, with freshwater
.090	56	
.086	100	
.068	28	128°F, inundated without fly ash, with freshwater, with Class C cement
.072	56	
.064	100	

Bond Strength (age 28 days, cured inundated at 128°F)

<u>Rock Type</u>	<u>Push-Out Bond (psi)</u>
Castile Anhydrite	375
Upper Anhydrite	274
Bell Canyon Sandstone	953

Figure 1. Simulated Borehole Specimen (SBS) for Push-out and Permeability Testing

Figure 2. Simulated Borehole Specimen (SBS) for BCT

TABLE 5

Proposed Field Salt Grout Mixture

<u>Proportions (wt%)</u>	<u>BCT-1F</u>
Class H Cement	50.1
Expansive Additive	6.7
Fly Ash	16.9
Salt (NaCl)	6.5
Dispersant	0.2
Defoamer	0.02
Water	19.5

<u>Properties</u>	
Water-Cementitious Material Ratio, by wt	0.26
Fluid Density (lb/gal)	17.2

development data were comparable to the WES DHT 1 (9) mixture data. Final developments, reported in Dowell's letter of July 31, 1979, are included in "Laboratory Development at Dowell, PSU, and ORNL."

During late April, the plug location for the BCT was selected to be in the anhydrite section above the sandstone layer. Boxes of anhydrite core were shipped from Carlsbad to WES and also to Pennsylvania State University (PSU), Oak Ridge National Laboratory (ORNL), and Dowell. At this time, the BCT-1F grout mixture was selected for the plug subject to final development testing and evaluation. Materials had previously been provided to PSU and ORNL so that all four laboratories would be using the same materials for the mixture.

Emphasis of the development work at WES was shifted to the BCT-1F mixture physical properties as follows:

1. Mechanical bond strength tests of grout/anhydrite interface in push-out specimens
2. Fluid and gas permeability of the SBS (push-out specimens)
3. Expansion and compressive strength tests
4. Curing temperature curve for simulated in situ plug location
5. Petrographic examinations.

Specimens for push-out bond strength testing were cast and cured in saturated salt (NaCl) brine at 128°F. These were the SBS specimens with the 4-inch-diameter anhydrite cores with center NX-sized drill holes filled with BCT-1F grout mixture. Companion test cylinders (3 x 6-in.) were cast at the same time and cured in the same environment with the push-out specimens. Data in Table 6 show uniformly high shear-bond strengths and unconfined compressive strengths.

TABLE 6

Push-Out Bond and Unconfined Strength for BCT-1F Grout

<u>SBS Specimen</u>		<u>Age (days)</u>	<u>Anhydrite Bond-to-Grout (psi)</u>		
1		30	1060		
2		30	980		
3		30	1070		
4		7	890		

<u>Specimen</u>		<u>Plastic Mixing Time (min)</u>	<u>Age at Test (days)</u>	<u>Unconfined Compressive Strength (psi)</u>	<u>Density (lb/ft³)</u>
<u>Cylinder Size</u>	<u>Number</u>				
6 x 12	1	120	7	5,235	--
3 x 6	1	3	30	7,215	125.4
3 x 6	2	60	30	8,555	124.2
3 x 6	3	120	30	8,910	124.2
3 x 6	4	120*	30	8,910	123.1

*Defoaming agent omitted

Permeability tests on the grout by itself had indicated a relatively small flow rate with freshwater, approximating a fraction of a microdarcy. However, permeability tests on the SBS samples with the grout-anhydrite interface, first accomplished on July 25 at 41 days' age, revealed almost immediate permeability along a path coincident with, and parallel to, the interface. Samples were about 5-inches long and were cured at laboratory ambient temperature. They were placed in double plastic bags immediately after casting, and a double layer of plastic coating was added to the exposed surfaces at age 1 day. A companion specimen of anhydrite without the grout-filled hole did not show any leakage (permeability less than 10^{-7} darcy). While preparing the first specimen for placement in the water permeability rig, a thin slice had been sawed, dry, from the top. There was

a visible white annular ring around the grout-anhydrite interface. This was studied further and is discussed in this report. Mechanical bonding of the grout was then tested by pushing the grout core out of the anhydrite cylinder surrounding it. Movement occurred at a shear-bond stress of 362 psi. This and subsequent tests showed that there was not a direct correlation between shear-bond strength and impermeability to freshwater along a salt grout-anhydrite interface.

Several Nalgene plastic vials were filled with BCT-1F grout and cured under a variety of environments for further petrographic study. Two additional SBS specimens were cast, and one was immediately placed under water simulating the chemical content of the groundwater at the WIPP site. The water was maintained at 90°F. The second specimen was protected in double plastic bags for the initial 24 hours after casting. It was then coated with a double layer of Protexo-Cote (plasticized) and double-dipped in hot wax before immersing in the simulated groundwater at 90°F. Data for restrained prisms (3 x 3 x 10 in.) cast at the same time and cured as indicated are listed in Table 7. Both SBS specimens were tested in the permeability rigs at 6 days' age, and both leaked water at the anhydrite-grout interface as soon as the pressure reached 40 psi. Mechanical bond of the grout to anhydrite was then tested by pushing the grout out of the surrounding anhydrite cylinder. The force required to cause movement at the interface gave a shear-bond stress for the area of the interface of 352 psi for the coated specimen and 372 psi for the uncoated specimen. These values are consistent with the earlier SBS specimen which had a resistance of 362 psi.

A number of variations of the basic BCT-1F mixture were studied in a short time in an attempt to reduce the permeability at the interface. One of the most promising was the omission of salt from the mixing water, and this mixture was later designated as BCT-1FF. Another promising mixture used a saturated solution of anhydrous sodium sulfate (Na_2SO_4) in water for the mixture water. At 7 days' age the sodium sulfate SBS specimen showed no evidence of leakage at the grout-anhydrite interface, and the compressive strength was 4700 psi.

TABLE 7

Restrained Expansion Data for BCT-1F

Mixture BCT-1-F

<u>Expansion (%)</u>	<u>Age (days)</u>	<u>Remarks</u>
0.000	2	Demolded at 32-1/2-hr age; double-coated with Protexo-Cote and wax; kept inundated in simulated groundwater at 90°F.
0.014	3	
0.037	9	
0.033	10	
0.040	11	
0.039	13	
0.040	16	
0.051	21	
0.068	28	
0.070	56	

Mixture BCT-1-F

<u>Expansion (%)</u>	<u>Age (days)</u>	<u>Remarks</u>
0.050	2	Demolded at 32-1/2-hr age; inundated in simulated groundwater at 90°F at time of casting and kept inundated between readings.
0.060	3	
0.069	9	
0.059	10	
0.070	11	
0.074	13	
0.061	16	
0.062	21	
0.073	28	
0.049	56	

The anhydrite rock at the proposed plug depth was examined for the possible presence of rock salt. The following material from hole AEC-7 was examined:

- a. Core 13, Box 226, depth interval 4493 to 4495.5 ft, 3-inch-long piece from 4493.0 to 4493.25 ft.
- b. Core 13, Box 228, depth interval 4498.0 to 4500.7 ft, two pieces, each about 4-1/2-inches long, and four trimmed ends, each about 1/2- to 1-inch long.
- c. Core 13, Box 229, depth interval 4500.7 to 4503.4 ft, 2.7 ft of core.

All of the rock looked like anhydrite without the presence of any recognizable rock salt. The 2.7-ft length of core did contain a bedding plane at 4502.2 ft; this was an open contact coated with a thin, black layer of what was probably a carbonaceous material. This may well have been an opening in the rock in the hole. Two thin zones of brownish dolomite about 6 inches below this bedding plane were present; they were about 1/8 to 1/4 inch thick.

Several samples of the rock were examined by X-ray diffraction. Several small diameter cores were taken and the ends trimmed and discarded to eliminate the contamination from the salt drilling mud. Only anhydrite and a small amount of dolomite were found. Soaking in distilled water, decanting, and drying the residue to precipitate any dissolved salt also showed no detectable salt by X-ray diffraction examination.

All of the development data were reviewed during a meeting at WES on August 14, 1979. Preliminary data for the freshwater grout showed a higher strength, reduction in the permeability at the interface of SBS specimens, and generally increased expansion of the test prisms. Push-out bond strengths in anhydrite cores were equal to or greater than for the salt grout. When split along the length of the specimen, the freshwater grout

samples showed a tighter adherence of grout to rock, and no discernible leakage paths. Some of the separation went through the grout (not at the interface), indicating a very good bonding of freshwater grout to anhydrite. The consensus at the meeting was that the freshwater grout mixture (Table 8) had acceptable properties and was the best choice for the BCT plug. Further testing was to be done at the three laboratories (WES, PSU, and ORNL) to confirm this decision. Results of the testing showed that the BCT-1FF freshwater grout was suitable for the BCT plug.

Several SBS samples were prepared late in August for permeability testing of the grout interface in anhydrite rock cores. Three curing conditions were used through about 10 days' age and are described at the bottom of Table 9. In all cases, the samples were immersed in brine water while the grout was still fluid and through about 10 days of curing. The samples were then placed in the permeability apparatus and subjected to freshwater at 200 psi applied to the grout-filled central and to about a 1/2-inch annulus of the anhydrite core. WES equipment for permeability is described in method CRD-C 48-78 of Reference 6.

TABLE 8

Freshwater Grout Mixture

<u>Proportions (wt%)</u>	<u>BCT-1FF</u>
Class H Cement	52.2
Expansive Additive	7.0
Fly Ash	17.6
Dispersant	0.2
Defoamer	0.02
Water	23.0
 <u>Properties</u>	
Water-Cementitious Material Ratio, by wt	0.30
Fluid Density (lb/gal)	16.5

TABLE 9

Water Permeability Tests BCT-1FF Grout Lab Samples

Age (days)	Water Permeability (10^{-6} darcy)		
	Curing Condition		
	1	2	3
25	2.26	13.1	0.88
50	1.37	3.3	0.73
82	1.49	2.09	0.56
110	2.25	4.12	0.73
210	2.84	4.76	0.58

Curing Conditions

1. Curing temperature to 150°F at 12 hours, reduced to 100°F at 24 hours, and remaining constant at 100°F through 10 days. Pressure of 1500 psi applied to fluid grout in the anhydrite core and confining ring through hardening and through 10 days' age.
2. Constant temperature of 100°F and pressure of 1500 psi applied to fluid grout through hardening and through 8 days' age.
3. Constant temperature of 100°F and ambient atmospheric pressure through hardening and through 10 days' age.

Permeability values are listed in Table 9. The sample under the third curing condition of constant 100°F temperature and ambient atmospheric pressure has maintained the lowest permeability values--less than 1×10^{-6} darcy through 210 days' age. The other curing conditions were included to attempt to bracket the downhole curing conditions for the field plug. The small sample size and grout in the annulus between the steel ring and the anhydrite core may not provide as much restraint as in the in situ field plug. Values of less than 5×10^{-6} darcy after 48 days and through 210 days' age for all three samples showed evidence of a tight contact between

the grout and anhydrite. Water permeability values for grout samples with the low water-cement ratio of 0.3 have typically been less than 1×10^{-7} darcy. These samples will continue to be tested at later ages.

Two restrained 3-inch prisms were cast, and the linear expansion data are listed in Table 10.

The solubility of anhydrite core from the BCT plug location and of reagent grade anhydrite was studied in distilled water and brine solutions by the Chemistry and Plastics Branch of the WES Structures Laboratory. The core was ground to pass a No. 100 sieve and dried at 105°C overnight before measuring the solubility of the material in different solutions. Some reagent grade anhydrite (anhydrous CaSO_4) was passed through a No. 100 sieve and dried overnight at 105°C . Three solutions were used to determine solubility. A 30% sodium chloride (30% by weight of water) was prepared by dissolving 900 g of sodium chloride in 3000 mL of distilled water. The WIPP site simulated groundwater^{4 5} and distilled water were also used.

TABLE 10
Laboratory Expansion Data BCT-1FF Grout Mixture

<u>Age (days)</u>	<u>Linear Expansion (%)</u>
4	0.024
5	0.026
6	0.038
8	0.045
11	0.030
13	0.042
21	0.038
56	0.020

NOTE: Prisms demolded at 17 hours' age and cured inundated in simulated groundwater at 90°F .

Two grams of the ground and dried anhydrite were weighed and placed into a 400-mL beaker containing a magnetic stirring bar. Two-hundred-fifty milliliters of the solution to be used were then added to the beaker. The beaker was then placed on a magnetic stirrer and mixed for 24 hours. The solution containing the portion of undissolved anhydrite was filtered through a tared Gooch crucible containing a glass fiber filter coated with asbestos. The crucible was dried at 105°C for 3 hours and then weighed to determine the weight of solids on the filter. All the filtrates were clear, and there was no evidence that any solids passed through the filter. The difference in weights between the 2 gm added and the amount on the filter was calculated to be the soluble portion of the anhydrite samples.

Reagent grade anhydrite was more than twice as soluble as the anhydrite core from the BCT plug zone (Table 11). The solubility increase in 30% NaCl solution compared with distilled water was about a 36% increase for the core pieces while reagent grade anhydrite increased about 270%.

Results of the chemical analysis of a piece of the same core used for the solubility tests are listed in Table 12. The fact that the anhydrite was more soluble in brine than in fresh (distilled) water was a significant factor in the decision to change from a saltwater to a freshwater grout for the BCT.

Studies were performed by the Petrography and X-ray Branch of the WES Structures Laboratory to aid in the discussions of whether to include salt in the mixing water for the BCT grout.

Pieces of core over the interval of 4493 to 4503-ft depth were examined for the possible presence of rock salt. There was no detectable salt in the core pieces that were examined. There were small amounts of dolomite, quartz, and plagioclase feldspar disseminated throughout the rock. Two seams of brownish dolomite and a bedding plane with an open contact coated with black carbonaceous material were present in the core at about 4502 feet.

TABLE 11
Solubility of Anhydrite Core

<u>Sample</u>	<u>Solution</u>	<u>Solubility (g/100 mL)</u>
Anhydrite Core	Distilled Water	0.115
Anhydrite Core	30% NaCl Solution	0.156
Anhydrite Core	Simulated Groundwater	0.125
Reagent Grade Anhydrite	Distilled	0.267
Reagent Grade Anhydrite	30% NaCl Solution	0.724

TABLE 12
Chemical Analysis of Anhydrite Core

	<u>Percent</u>
Volatiles	22.09
SO ₃	24.88
MgO	9.40
CaO	41.67
Al ₂ O ₃	0.11
K ₂ O	0.04
NaO	0.17
SiO ₂	0.86
NaCl*	0.14

*The core was drilled with saltwater mud.
Therefore, the sample was probably contaminated
with NaCl.

Phase composition of BCT-1F saltwater grout and the proposed BCT-1FF freshwater grout were determined by X-ray diffraction, Table 13. Variables included in the study were temperature, 78° to 128°F; type of curing, wet or dry; and the use of salt or fresh mixing water in the grout. The work showed that there was a significant difference in phase composition depending on whether saltwater was used. For freshwater grout there was the usual formation of 6-calcium aluminate trisulfate-32-hydrate (ettringite). For saltwater grout tetracalcium aluminate dichlorid-10-hydrate (chloroaluminate) tended to form instead of some of the ettringite. For saltwater grout there was no significant effect for temperatures of 78° to 93°F. At 128°F there was less ettringite and more chloroaluminate. Extended wet curing after 4 days resulted in more ettringite and chloroaluminate, and the chloroaluminate was better crystallized. General similarities in phase composition were observed for BCT-1F compared to saltwater grouts from ERDA-10 and the 17-year-old sample from Duval Mine.^{4 7}

During the early efforts, several specimens (SBS) having grout-to-anhydrite contacts with different curing conditions were examined to evaluate the condition of the contacts. Five specimens with holes in anhydrite cores filled with BCT-1F saltwater grout were cured at different temperatures and moisture environments (Tables 14 and 15). Each of these specimens had a

TABLE 13
Phase Composition of Grout (4 days' age)

<u>Crystalline Phases</u>	<u>Saltwater Grout BCT-1F</u>	<u>Freshwater Grout BCT-1FF</u>
Chloroaluminate	Major	Absent
Calcium hydroxide	Major	Major
Ettringite	Minor	Major
Hard-dried monosulfoaluminate	Very minor	Absent
Unhydrated portland cement	Moderate	Moderate
Halite	Moderate	Absent
Quartz	Minor	Minor
Gypsum	Absent	Minor

TABLE 14

Petrographic Examination of Contact Surfaces of Anhydrite Rock
to BCT-1F and BCT-1FF Grout on Permeability Specimens Kept in Dry Storage

Specimen No. 1

Age - 41 days

Cast - June 14, 1979, using saltwater grout BCT-1F

Treatment - Wrapped in double plastic bags for 24 hr, then Protexo-Coted and stored in same bags. All at ambient temperature.

Observations - There is a crack between the grout and the anhydrite measuring 0.18 mm* wide. The most conspicuous white halo is seen in this sample. This sample is a slice from the top of the specimen and was sawed dry. Figures 2 and 3 illustrate this specimen before the test.

Specimen No. 2

Age - 64 days

Cast - May 24, 1979, using saltwater grout BCT-1F

Treatment - Immediately placed in 93°F environment, uncovered, and left for 64 days.

Observations - The crack width at the contact measured 0.3 mm.* No detectable halo was present. When tensile splitting pressure was applied to the specimen the rock broke free along the contact leaving the grout core intact. Flattened clumps of crystals were evident on the grout surface. Material from this surface was examined by X-ray diffraction. The material was a mixture of grout and rock constituents.

Specimen No. 3

Age - 7 days

Cast - July 27, 1979, using freshwater grout BCT-1FF

Treatment - Same as Specimen No. 1

Observations - Specimen was broken in tensile splitting after test. No crack was detected along the exposed contact. The good bond along this contact is shown in Photo 2; the lack of

TABLE 14--Continued

Specimen No. 3--Continued

bond at a contact of rock and grout is also shown in this photograph. Although this specimen leaked during permeability testing it is believed this was due to a curvilinear crack through the length of the grout. There was no detectable halo.

TABLE 15

Petrographic Examination of Contact Surfaces of Anhydrite Rock
to BCT-1F Grout on Permeability Specimens That Were Wet Cured--
All Cast on July 28, 1979

Specimen No. 4

Age - 4 days

Treatment - Cured in simulated brine water at 90° to 93°F. A horizontal slice was cut in a water-cooled saw.

Observations - There was a crack along the contact; its width was 0.03 mm.* There was a slight white halo around the contact on the top surface of the specimen.

Specimen No. 5

Age - 4 days

Treatment - Sealed in double plastic bags overnight at ambient temperature, then protexo-coated and waxed and placed in 90° to 93°F brine water. A horizontal slice was cut wet as above.

Observations - There was a crack along the contact; its width was 0.03 mm.* A slight white halo was evident.

Specimen No. 6

Age - 5 days

TABLE 15--Continued

Specimen No. 6--Continued

Treatment - Same as Specimen No. 5; this was an adjacent slice to it. The difference was having a fracture surface which was made with a pipe cutter.

Observations - There was a crack along the contact with a width of 0.03 mm.* No white halo was seen. Crystals could be seen growing along contact between grout and anhydrite. Needle-like crystals projected from the grout toward the anhydrite. Small patches of grout remained intact to the anhydrite.

*Measurement made at 60X

crack along the contact between the grout and anhydrite measuring 0.03 to 0.3 mm in width. Figure 3 shows the surface of a specimen at 41 days' age after being sawed dry to expose a fresh surface. An enlargement of the small area of contact enclosed in the box in Figure 3 is shown in Figure 4. White halos which were present on some sawed surfaces of specimens were always present on the anhydrite side of the contact. When the contact surface was exposed by fracturing (such as tensile splitting), no halo was found on any surface. There was a thin white line on each fracture surface which appeared to be scarring of the rock during coring. No gypsum was detected in the white powder from a typical halo. It was composed of the anhydrite rock, probably as sampling contamination, and salt which had precipitated from water during evaporation on this surface. For the saltwater grouts the crack width was greater for the two specimens cured dry than the three specimens that were wet cured. The halo on the sawed surfaces was probably a result of the sawing process.

The single specimen made with BCT-1FF freshwater grout exhibited a tight contact of grout to anhydrite with no visible crack. The fracture during tensile splitting traveled through the grout rather than at the contact interface, indicating a good bond. Figure 5 compares contact surfaces of a sample of freshwater grout on the left and the saltwater grout on the right

Figure 3. Sawed surface of BCT-1F saltwater grout filling hole in anhydrite core, 0.9X.

Figure 4. Enlargement of small indicated area of Figure 2, 18X.

Figure 5. Fracture surfaces of freshwater BCT-1FF grout and saltwater BCT-1F grout. On left is example of 7-day-old freshwater grout placed in contact with anhydrite rock. Some of the separation went through the grout indicating good bond. On right is example of 45-day-old saltwater grout placed in contact with same rock. There was complete separation along this contact when tensile splitting pressure was applied.

after tensile splitting. Complete separation occurred at the contact for saltwater grout when the tensile splitting pressure was applied.

Considerable additional work was done as a part of the ongoing FY '80 Geochemical Program and will be reported separately. The later work has emphasized the importance of keeping specimens wet at all times, of keeping confining pressure on the specimens to prevent stress relief cracking to minimize damage and disturbance during cutting, and the general desirability of examining fractured surfaces and of making observations of these contact surfaces with a stereomicroscope.

This SBS type of specimen is used to study the structure along the contact of grout to rock and its relation to permeability. Examination of specimens before and after permeability testing can serve to characterize the contact before testing and determine if it changed during testing. A sawed surface of a SBS with BCT-1F saltwater grout is shown in Figure 6. When the metal restraining ring was removed, the anhydrite rock cracked (radially) in several places within a few hours because of stress relief. The grout is not cracked. Its "marbled" appearance was caused by pouring the grout through brine water standing in the center hold and in the annulus between the rock and metal ring. The white lines are believed to be regions of higher water content or of salt concentration. A fracture surface of the same specimen with the metal restraining ring still in place is shown in Figure 7. The anhydrite rock did no crack.

A portion of the contact of grout and anhydrite and a sawed surface of another SBS is shown in Figure 8. With the metal restraining ring still in place, there is no cracking. From XRD evidence the white material at the contact contained some gypsum (hydrated calcium sulfate). If so, it indicates some dissolving of the anhydrite rock and later precipitation of gypsum at the contact surface. The same sample as in Figure 8 is shown in Figure 9 after overnight drying at 140°F. A prominent crack at the contact can be seen. Several radial cracks are present in the grout at locations indicated by the arrows.

Figure 6. Sawed Surface of SBS Specimen with Restraining Ring Removed

Figure 7. Fractured Surface of SBS Specimen with Restraining Ring in Place (X0.7)

Figure 8. Portion of Figure 7 Before Drying (X0.6)

Figure 9. Same as Figure 7 after Overnight Vacuum Drying (X0.6)

XRD work has shown that penetration of chloride into the BCT-1FF freshwater grout during storage of SBS specimens under brine is limited to the upper 1/4 inch of the specimen in the samples which have been examined.

Laboratory Development Work at Dowell, PSU, and ORNL

Dowell Regional Laboratory, Midland, TX

The Dowell Regional Laboratory at Midland was requested to run thickening time and compressive strength tests on the proposed salt cement system for the BCT plug. This work resulted in the BCT-1F grout mixture. Thickening time tests were performed in a pressurized consistometer according to API schedule 5 (Reference 8). All seven mixtures had 70% Lone Star H cement, 30% fly ash, 30% salt, 10% expansive additive and varying amounts of dispersant D65. The results are listed in Table 16. Sample cubes for three mixtures were cast and cured at 128°F. Compressive strengths through 28 days' age are listed in Table 17.

Following the selection of the BCT-1F grout mixture the Dowell Laboratory at Midland conducted expansion, compression, and shear-bond tests on the grout set inside anhydrite cores. All samples were cured at 128°F and at atmospheric pressure.

Expansion tests were conducted using length comparometer and cement specimens 1 x 1 x 11-1/4 in. (10-in. effective length). Specimens were stripped from the molds after 15 hours curing and initial length measurements were made. Average expansion data for the bars are listed in Table 18. Compressive strength measurements were performed on 1-in.-diameter cylinders. The data are listed in Table 19.

The 4-in.-diameter anhydrite core sample was sawed into 1.12-in. slices for the shear-bond strength tests. A 1.30-in.-diameter hole was carefully cut in each core slice. The core slice was placed on a greased brass plate, and grout was poured into the hole. Special care was taken to remove entrapped air. A second greased brass plate was placed over the slice, and

TABLE 16

Thickening Time Test Results

<u>No.</u>	<u>Dispersant (%)</u>	<u>Fluid Wt (lb/gal)</u>	<u>Yield (ft³/5K)</u>	<u>Water (gal/5K)</u>	<u>Thickening Time (hr:min)</u>
1	0	17.0	1.05	3.45	1:27
2	1.0	17.5	1.0	3.03	4:20
3	0.85	17.5	1.0	3.03	1:00
4	0.75	17.0	1.05	3.45	6:07
5	1.0	17.0	1.05	3.45	5:46
6	1.75	18.0	0.93	2.65	5:02
7	0.3	17.0	1.05	3.45	3:12

TABLE 17

Compressive Strength Test Results

<u>No.</u>	<u>Age</u>				
	<u>12 hr</u>	<u>24 hr</u>	<u>72 hr</u>	<u>7 day</u>	<u>28 day</u>
2	25	620	3201	3738	3226
6	25	423	2893	3658	5265
7	25	975	2958	3413	2795

TABLE 18

Dowell Expansion Data for BCT-1F Grout

<u>Age</u>	<u>Linear Expansion (%)</u>
15 hours	Initial
2 days	.024
7 days	.027
14 days	.038
28 days	.048

TABLE 19

Dowell Compressive Strength Data for BCT-1F Grout

<u>Age (days)</u>	<u>Compressive Strength (psi)</u>
7	3370
14	3850
21	4130-6380*
28	4650

*NOTE: Specimen broke longitudinally, yet continued to take load. First number shown is the point where first failure occurred, and second number is point of complete failure.

the cores with grout were cured in a saltwater bath at 128°F. Force required to extrude the cement plug from the core slice was measured by loading the grout using a 1-in. plug with a plate with a 1.38-in. hole under the core slice. Shear bond data are listed in Table 20.

Following the meeting at WES in August 1979, the Dowell Laboratory at Midland tested the BCT-1FF freshwater cement system including X-ray diffraction and optical emission spectrographic analyses. Compressive strengths were 6240 psi for samples cured in water and 4765 psi for samples cured in air. Permeability to freshwater was 10×10^{-6} darcy for a water-cured specimen and 190×10^{-6} darcy for an air-cured specimen. X-ray diffraction and optical emission spectrographic analyses were identical for water-cured and air-cured specimens and are given in Table 21.

Pennsylvania State University

Along with the borehole plugging cement studies at the Materials Research Laboratory of Pennsylvania State University, six studies were performed in support of the grout development for the BCT. Results were reported to SNL by letter, and some were included with data at later curing ages in references.^{9 10} The results are included in this section.

TABLE 20

Dowell Shear Bond Data for BCT-1F Grout

<u>Age (days)</u>	<u>Shear Bond Strength (psi)</u>
7	414 ^a
14	750 ^b
28	430 ^a

NOTES: ^aAnhydrite core sample broke before cement-to-anhydrite bond was broken.

^bCore sample broke simultaneously with breaking of bond.

TABLE 21

Dowell BCT-1FF Analyses

I X-Ray Diffraction Analysis

<u>Major</u> <u>(25-100%)</u>	<u>Minor</u> <u>(10-30%)</u>	<u>Low</u> <u>(Less than 15%)</u>	<u>Possible Low</u> <u>(Less than 15%)</u>
Amorphous	-----	Alite, Portlandite Ettringite	Calcite

II Optical Emission Spectrographic Analysis

<u>Major</u> <u>(10-100%)</u>	<u>Minor</u> <u>(1-10%)</u>	<u>Trace</u> <u>(Less than 1%)</u>
Calcium	Aluminum	Lead, Manganese,
Silicon	Sodium	Barium, Vanadium,
	Magnesium	Lithium, Copper,
		Titanium, Nickel,
		Strontium, Zirconium

Three formulations of grout were investigated (Table 22). One-inch-diameter by 2-in.-long cylindrical samples of the BCT-1F and BCT-1FF formulations were prepared for testing. The BCT-1F samples were cured in 95% plus relative humidity and the BCT-1FF in WIPP-A brine (simulated groundwater). Curing temperatures were 81°F, 140°F, and 194°F. Bulk density, microhardness, compressive strength, and X-ray diffraction tests were performed on the specimens as they matured. Samples for both formulations were mixed according to API standard procedures, poured into glass shell-vials, and allowed to cure for a few days until solid enough to break the glass away. At this point, the samples were returned to their sealed jars and allowed to continue curing (high R.H. and WIPP-A brine, respectively).

Results of bulk density, microhardness, and compressive strength measurements for the two formulations are given in Tables 23 through 26. Microhardness for BCT-1F shows a gradual increase with time. The data for

TABLE 22

PSU Grout Formulations

	BCT-1F		PSU Salt-Free		BCT-1FF	
	Wt (g)	Wt% Solids	Wt (g)	Wt% Solids	Wt (g)	Wt% Solids
Solid						
Cement H	592	62.4	271.8	68.0	66.6	68.0
Fly Ash	200	21.1	91.8	23.0	22.4	22.9
Exp. Add	79.2	8.4	36.4	9.1	8.9	9.1
Salt (NaCl)	77.2	8.1	--	--	--	--
D-65	2.4	--	0.9	--	.3	--
Liquid						
D-47	0.2	--	0.1	--	--	--
Water	261.4	--	99.0	--	29.4	--

TABLE 23

Density Measurements (g/cm³)

<u>Temp (°F)</u>	<u>Hydration (days)</u>			
	<u>BCT-1F</u>			<u>BCT-1FF</u>
	<u>14</u>	<u>28</u>	<u>56</u>	<u>7</u>
81	2.11	2.07	2.09	2.15
140	2.09	2.11	2.15	--
194	2.10	2.11	2.07	2.11

TABLE 24

Microhardness (kg/mm²) ±

<u>Temp (°F)</u>	<u>Hydration (days)</u>			
	<u>BCT-1F</u>			<u>BCT-1FF</u>
	<u>14</u>	<u>28</u>	<u>56</u>	<u>7</u>
81	30.99 ± 4.2	25.48 ± 4.7	52.70 ± 7.85	63.89 ± 10.30
140	31.96 ± 3.0	42.52 ± 8.8	52.54 ± 3.30	98.06 ± 20.04
194	46.03 ± 12.9	43.31 ± 7.9	49.04 ± 7.35	74.89 ± 10.61

TABLE 25

Compressive Strength of BCT-1F (Ksi)

<u>Age (days)</u>	<u>Curing Temperature (°F)</u>		
	<u>81</u>	<u>140</u>	<u>194</u>
14	7.1	9.2	6.7
28	9.2	9.5	8.7
56	8.8	7.0	5.0
90	11.5	10.3	10.3
180	11.7	11.2	8.5

TABLE 26

Compressive Strength of BCT-lFF (Ksi)

Age (days)	Curing Temperature (°F)			
	81	95	140	194
7	11.3	13.1	13.4	7.4
14	8.8	17.7	10.9	6.1
28	13.3	17.8	15.5	7.6
56	12.5	17.1	18.6	7.8
90	18.3	12.4	13.8	6.7

compressive strengths of the BCT-lF grout mixture indicate a gradual reduction of strength between 28 and 56 days at the two highest curing temperatures (far above the field BCT plug environment). Compressive strengths of the freshwater BCT-lFF grout are significantly stronger than the BCT-lF grout at all ages and curing temperatures. The observed strengths were fairly consistent with similar trends except for the continuing increase of strength between 56 and 90 days for the curing temperature of 81°F. At a stage of hydration, up to 180 days, the strengths generally increased, reaching maximum values at about 140°F. Above 140°F, however, strengths were reduced, below the strengths at 81°F at all ages. Physical deterioration of samples cured in WIPP-A brine at 194°F for 90 days occurred. Incrustations of $Mg(OH)_2$ and Friedel's salt were observed on the surfaces of samples. The curing of the expansive cement grout samples without restraint may explain some of the deterioration at elevated temperatures.

X-ray diffractograms generally confirmed the trend of greater reaction at higher temperatures at a specific length of cure (Table 27). For BCT-lF, β - C_2S (belite) appeared to be present in all of the samples ($\sim 32^\circ 2\theta$) while Friedel's salt $\frac{1}{2}C_3A(CaCl_2)H_{10}$ appeared in the 140°F and 194°F samples for both the 14- and 28-day curing periods. Portlandite was only observed at 81°F and 14 days and ettringite only at 81°F and 28 days. A broad reflection centered at about $29.5^\circ 2\theta$ was tentatively

TABLE 27

X-Ray Diffraction Results
(decreasing order of abundance)

Temp (°F)	BCT-lF		BCT-lFF*
	14 days	28 days	7 days
81	Portlandite β -C ₂ S Calcite	Ettringite β -C ₂ S Calcite	β -C ₂ S Ettringite Gypsum Quartz Tr Calcite
140	Friedel's salt β -C ₂ S Calcite	Friedel's salt β -C ₂ S Calcite	β -C ₂ S Ettringite Gypsum Quartz
194	Friedel's salt β -C ₂ S Calcite	Friedel's salt β -C ₂ S Calcite	β -C ₂ S Friedel's salt Quartz Gypsum Tr Ettringite

*These samples cured in WIPP-A brine

All samples also contain amorphous C-S-H.

identified as calcite. The results for BCT-lFF indicated that with the removal of NaCl, ettringite, and gypsum are stable phases relative to Friedel's salt. The amounts of gypsum and ettringite appeared to be diminishing with increased curing temperature. In BCT-lF, Friedel's salt was identified in samples cured at 140°F and 194°F. In the freshwater BCT-lFF there was less ettringite at the highest temperature than at the lower temperatures. At 90 days, there seemed to be more C-S-H present in the BCT-lFF sample cured at 81°F than in the higher temperature samples.

Apparent viscosities were measured at 77°F on a Haake Rotovisco RV3 rotational viscometer at a succession of times up to 5 hours. The apparent viscosities measured at 150 and 600 rpm are listed in Table 28. The control sample was water and cement with no additional components but at the same w-c ratio. Standard API mixing procedure was used excluding the 6.5-minute measurement and including 20 minutes of mixing at 100 rpm. The remaining measurements, made about every hour, included mixing at 100 rpm between measurements.

The BCT-1F mixture was antithixotropic up to the first hour measurement. The control (Class H cement and water) was antithixotropic whereas the mixture without salt was thixotropic. The extent of thixotropy and antithixotropy was relatively minor up to 4 hours of mixing.

The permeability of anhydrite to gas was essentially nil and therefore was assumed to be impermeable to water in the present time frame. Water permeability of solid samples of BCT-1FF cast in steel rings was very low--no flow at 1 week, 2×10^{-7} darcy at 2 weeks, and no flow at 4 weeks. The curing temperature for the solid samples was 95°F. Applied pressure of deionized waters varied from 0 to 450 psi.

TABLE 28

Apparent Viscosity Measurements (C_p)

Time After Initial Mixing	BCT-1F		PSU Salt Free		Control	
	150 rpm	600 rpm	150 rpm	600 rpm	150 rpm	600 rpm
6.5 min	180	155	60	45	220	100
0.5 hr	300	218	90	70	220	125
1.0 hr	460	244	190	90	370	130
2.0 hr	--	--	270	100	475	155
2.5 hr	665	296	--	--	--	--
3.0 hr	--	--	305	135	710	290
4.0 hr	--	--	340	165	mixture set	
4.5 hr	--	--	340	170	--	--
5.0 hr	1215	344	--	--	--	--

Permeability data for samples of BCT-1FF grout in anhydrite cores (2-in. OD and 3/4-in. ID) are presented in Table 29. Specimen length was about 1.4 in., and the anhydrite core was from the 4350 to 4500-ft depth in AEC 7 hole. Deionized water permeabilities for samples cured 1 to 3 weeks at 95°F were in the 10^{-6} to 10^{-5} darcy range. However, by 4 weeks, no flow was detected in two replicate samples after 29 to 50 hours at 610 to 640 psi.

Push-out/bond strengths were measured for both the PSU-salt-free and BCT-1FF mixtures. Samples were cured in anhydrite cores (2-in. OD and 3/4-in. ID), taken out of the 95°F curing chamber, measured and pushed-out

TABLE 29

Water Permeability of BCT-1FF Samples Cast in Anhydrite Cores^a

Curing Time (wk)	Elapsed Time Between Cure and Test (days)	Time of Test (hrs)	Water Pressure (psi)	Permeability (10^{-6} darcy)	Comments
1	1	41	400	1.5	Linear flow rate
2	3	8	400	2.2	Increasing flow rate value at 20 hrs
2	5	9	400	7.0	Increasing flow rate value at 112 hrs
3	1	21	400	22.0 ^b	Decreasing flow rate value at 7 hrs
3	2	90	400	2.3 ^b	Linear flow rate
4	12	29	640	< 0.25 ^c	Maximum value
4	31	50	610	< 0.16 ^c	Maximum value

^aSpecimens prepared using modified API mixing procedures, vibrated for 60 seconds, cured at 95°F in WIPP-A brine

^bSpecimens cured at 95°F in saturated air environment

^cEssentially impermeable under experimental time and pressure conditions. However, a maximum permeability value was calculated assuming a hypothetical 1-mL flow in the given time period.

in a special fixture at a rate of 0.025 in/min. Data obtained are summarized in Table 30. The bond-strength values increase with time and are considered to be very adequate. The bond strength of cement grout to anhydrite is likely to be the result of increased formation of the expansive component, ettringite in the cement, causing a greater stress to be exerted by the cement against the wall rock.¹¹

Oak Ridge National Laboratory

Laboratory evaluations of several borehole plug formulations proposed for the BCT were made by the Chemical Technology Division of Oak Ridge National Laboratory. The results reported in this section are extracted from Reference 12. ORNL tested six formulations (Table 31) using dry materials planned for the BCT plug (previously described). Plug-wall rock bonding and permeability studies were included using core sections of anhydrite from the AEC-7 drill hole at the 4382-ft depth.

The initial series of grout mixtures was made to determine the effect of fly ash composition, cement type, and water-reducing agents. Materials used were two samples of lignite fly ash from Dowell with different compositions, Type I and Class H portland cement, and a plasticizer or water-reducing admixture. The compressive strength results for Formula 1 showed no significant changes through 28 days' age for differences in cement, fly ash composition, or water-reducing agent. The curves were typical, showing a rapid increase in strength during the first 3 days and a slower increase over the remaining time.

Since the Formula 1 mixtures had excess water, additional mixtures (Formula 3 and 4) were made with a reduced water content. The compressive strengths of these mixtures at 28 days' curing age are compared in Table 32. Mixtures with the reduced water-cementitious ratio showed a higher strength (as expected).

Formula 2 (Table 31) was the same as Formula 1 but included an expansive additive. The expansive additive caused no change in permeability

or density. Specimens of the two formulations showed only the usual variation except for compressive strength which increased with curing temperature and age (Table 33 and 34).

TABLE 30
PSU Push-Out/Bond Strength Data

<u>Mixture</u>	<u>Curing Time (days)</u>	<u>Push-Out Bond Strength (psi)</u>
PSU Salt Free	4.75	1043
	4.75	843
BCT-1FF	7	704
	14	1030
	28	2059

TABLE 31
ORNL Composition of Borehole Plug Formulations

Proportions (wt%)	<u>Formulation No.</u>					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5 (BCT-1F)</u>	<u>6 (BCT-1FF)</u>
Class H Cement	50.8	46.7	57.2	57.8	48.6	52.2
Fly Ash	17.2	16.4	19.4	19.6	16.6	17.6
Expansive Additive	--	4.9	--	--	6.6	7.0
Salt	7.4	7.4	8.3	8.4	6.4	--
Dispersant	--	--	--	0.1	0.2	0.2
Defoaming Agent	--	--	--	.017	--	--
Water	24.6	24.6	15.1	14.0	21.6	23.0
Water-Cementitious Material						
Ratio, by wt	.36	.36	.20	.18	.30	.30

TABLE 32

Compressive Strength Data^a

Formula No.	w-c Ratio	Compressive Strength (Ksi)	
		7 days	28 days
1	.36	4.8	8.1
3 ^b	.20	9.4	11.7
4 ^c	.18	8.7	10.3

^aAll specimens wrapped in impervious film at ambient temperature 72° to 77°F

^bMeasured slump of k = 5.0 and workability of W = 2.25

^cWith 0.1 Plastiment added

TABLE 33

Physical Properties at 28 Days' Age

Formula No.	Curing Temp (°F)	Compressive Strength (Ksi)	Permeability (darcy)	Dry Density (g/cm ³)
1	72	5.2	2.5×10^{-4}	1.66
	104	8.7	2.0×10^{-4}	1.70
	131	9.3	1.6×10^{-5}	1.70
	185	8.4	1.2×10^{-4}	1.70
2	72	4.6	--	1.67
	104	6.8	3.0×10^{-5}	1.70
	131	8.7	2.5×10^{-5}	1.66
	358	9.7	3.6×10^{-7}	--

TABLE 34

Physical Properties at 91 Days' Age

Formula No.	Curing Temp (°F)	Compressive Strength (Ksi)	Permeability (darcy)	Dry Density (g/cm ³)
1	72	8.0	8.0×10^{-5}	1.68
	104	11.0	1.0×10^{-4}	1.72
	131	8.6	2.8×10^{-5}	1.69
	185	9.6	8.0×10^{-5}	1.72
2	72	6.7	1.4×10^{-4}	1.64
	104	9.7	--	--
	131	8.8	2.7×10^{-5}	1.68
	185	10.6	9.6×10^{-5}	1.66

Formula 5 was the BCT-1F saltwater grout. Formula 6 was the BCT-1FF freshwater grout. ORNL permeability measurements using WIPP brine were quite promising. Miniature boreholes were formed by coring 1-in.-diameter holes in the 4-in.-diameter anhydrite core samples. Slices of the cored samples 1-in. thick were filled with the grout mixture for push-out tests. The 1-in. anhydrite cores left from the above operation were bored still smaller to make smaller plugged boreholes of 1/2-in. diameter by 1-in. long for permeability measurements. Permeabilities were measured by ORNL standard procedures.¹³

Physical properties of plug and plug-rock combinations made with Formulas 5 and 6 are given in Table 35. Push-out bond strengths ranged from 360 to 780 psi with no distinct difference as a function of curing time or mixture composition. Nitrogen permeabilities of dried specimens of the BCT-1F grout mixture ranged from 1×10^{-7} to 2×10^{-6} darcy. The sample of grout in the anhydrite wall rock (without a microfracture) had a lower liquid permeability of 4×10^{-9} darcy. The BCT-1FF grout mixture had higher permeabilities associated with the interface between grout and

TABLE 35

Results of Plug/Rock Experiments

Formula	Curing Temperature (°F)	Curing Time (days)	Push-Out Strength ^a (psi)	Compressive Strength (Ksi)	Permeability (darcy)		
					Plug/Wall (Liq.)	Interface (N ₂)	Plug Solid ^b (N ₂)
5 (BCT-1F)	72	7	540	3.9	1.3×10^{-3c}	--	21.1×10^{-6}
	--	14	720	5.2	4.0×10^{-9}	--	5.0×10^{-7}
	104	7	360	6.4	--	--	1.0×10^{-7}
	131	7	450	8.6	--	--	1.7×10^{-7}
		14	360	9.9	3.1×10^{-6}	--	1.9×10^{-6d}
6 (BCT-1FF)	72	7	390	--	2.6×10^{-5}	3.0×10^{-4}	--
		14	780	--	1.1×10^{-3}	1.0×10^{-3}	--
	104	7	540	--	3.7×10^{-4}	2.1×10^{-4}	--
		14	510	--	1.4×10^{-3}	1.0×10^{-3}	--
	131	7	550	--	4.0×10^{-4}	1.2×10^{-4}	--
		14	520	--	2.0×10^{-5}	4.4×10^{-4}	--

anhydrite wall rock. A series of photo micrographs showed circumferential cavities at the interface which probably accounted for the increased permeability. The grout mixture was reported to be "thin and watery" for these permeability specimens. The excess water may have increased the dissolution of anhydrite at the interface. More research and development is needed to determine the interaction between grout and anhydrite wall rock and to reduce the permeability at the interface.

Field Operations During Plugging

Field mixing of cement grout for the two BCT plugs took place on September 26, 1979, and February 14, 1980. Although the actual volume for each short plug length was less than 10 ft³, batching and mixing operations were standardized for a volume of 200 sacks (cement plus fly ash), yielding about 190 ft³ of cement slurry. These mixing operations were used as trials in the development of quality control procedures for future and larger plugs.

The dry materials were batched and blended at the Dowell plant in Artesia, New Mexico, the day before they were mixed at the site. The batch plant was inspected by Sandia and WES personnel, and calibration dates of scales and equipment were documented. A sample of each of the materials in the grout mixture was obtained, and sources and dates of shipment were recorded. Members of the WES staff closely monitored the weighing, blending, and loading of the dry materials into one tier of a bulk truck for transport to the site.

The grout was mixed on-site in one tank of a twin-tank paddle mixing system with a 225 ft³ capacity. Carlsbad city water was pumped into the tank and used as mixing water. The dry material was added, and the final amount of water was added during mixing for proper viscosity of the slurry. Final fluid density for both mixing operations was 17.6 lb/gal. Density, slurry temperature, air control, and time of flow through a flow cone were

measured periodically for 3-1/2 hours. Grout slurry properties remained suitable for pumping (as measured by the flow cone) for 3-1/2 hours.

Weight percentages of components of the grout mixtures for the two field operations and laboratory development are listed in Table 36. Planning for field mixing has always involved using the minimum amount of water to achieve maximum density and suitable flow characteristics of the grout slurry for adequate pumpability. Resulting water-cementitious ratios were 0.276 and 0.273 for the field mixtures compared to 0.30 for the laboratory mixture. Batching of about 10 tons of dry materials resulted in normal slight differences in the amount of each component as noted in the table. This slight variation is within acceptable quality control limits. Uniform fluid densities for the two field-mixing operations attest to the successful control of batching of dry materials.

TABLE 36
BCT-1FF Grout Mixtures

Components	Proportions (wt%)		
	Lab	Field 9/26/80	Field 2/14/80
Class H Cement	52.2	53.1	52.7
LITEPOZ*3 Cement Extender (Fly Ash)	17.6	18.1	18.2
Expansive Additive	7.0	7.1	7.5
Dispersant (D65)	0.2	0.1	0.2
Defoamer (D47)	0.02	0.02	0.02
Water	23.0	21.6	21.4
<u>Properties</u>			
Water-Cementitious Material Ratio, by wt	0.30	0.276	0.273
Fluid Density (lb/gal)	16.5	17.6	17.6

*Trademark of The Dow Chemical Company

A dump bailer was used to place about 3 ft³ of grout slurry at the plug location for the September 1979 placement.¹⁴ Preparation of the hole was limited to circulation and replacing all of the brine fluid in the hole with clean brine water before placing the packer assembly and sand. However, when a few feet of sand was removed the day before plugging operations, a black sediment was present which apparently resulted from continuing corrosion of tubing in the hole. Table 37 lists the chemical analysis of water from the hole and the black filtered residue. The dump bailer was filled with slurry and lowered to the sand surface. It was raised about 1 ft, and the frangible glass nose window was broken, allowing the grout to flow out and displace the brine water upward. The 3 ft³ should have formed a plug about 6.8-ft long. Measurements have indicated that the plug length was about 6 ft.

A more normal cementing operation was selected for the plug addition in February 1980. While the grout was being mixed, the hole was prepared by circulating clean brine through tubing until it replaced all the fluid in the hole. The bottom of the tubing was located about 1 ft above the top of the first plug. After completion of circulating the hole, about 112 ft³ each

TABLE 37

Water and Filtered Residue Analysis

Water Analysis		Filtered Residue	
	(mg/L)		(wt%)
Ca	4579	CaO	5.90
Fe	16	Fe ₂ O ₃	31.6
K	1040	Na	8.8
Mg	1282	K	0.1
Na	120600	SiO ₂	2.7
SO ₄	1553	Cl	17.9
Cl	194300	Mn ₂ O ₃	0.2
Mn	15	Al ₂ O ₃	0.6
Sulfide	0.4	Volatiles at 550°C	7.9
		Volatiles at 850°C	6.5

of a chemical wash and spacer (to suspend solids) designed by Dowell were pumped down the tubing immediately followed by about 67 ft³ of grout slurry at a slow rate of about 11 ft³/min. The grout slurry was displaced with about 96 ft³ of brine water to equalize the level of grout in the tubing and annulus. After raising the tubing 20 ft, the excess grout above that depth was circulated out by pumping brine water down the tubing and forcing the excess slurry up the annulus. The hardened second plug extension is about 12-ft long instead of the intended 18 ft, presumably due to excessive washout during the displacement operation.

Members of the WES staff cast a large number of expansion prisms, cylinders, and cube specimens for strength and other physical properties. Specimens were cured in a tank of brine water obtained during circulating the hole. Lack of a temperature control for the heater during September 1979 allowed fluctuations of as much as 18°F below the intended temperature of 100°F overnight. Also, during the first 24 hours the temperature in the tank reached a peak of about 160°F because of the heat generated by the hydration of the tightly packed samples. Water temperature in the tank in February 1980 was more closely controlled after the first 24 hours to within $\pm 4^\circ$ of the intended 100°F. Also, the temperature during the first 24 hours reached a peak of only about 120°F by using a larger tank, a cooler starting temperature, and by removing the insulation overnight. Expansion prisms were measured daily. Some compressive strength testing of samples at early ages was done at the site on a portable testing unit in February. Samples were shipped by truck to the WES Structures Laboratory at 7 days' age for the first plug and 21 days' age for the second.

Laboratory Evaluation of Field Samples

When the field samples arrived at the WES Structures Laboratory, they were unpacked and placed in brine water and kept at 100°F. These samples are included in the long-term durability studies.

Unconfined compressive strength data in Table 38 include the early age testing of the February plug specimens. Strengths for the two plugs are about the same through 56 days' age. The second plug specimens show a greater increase in strength at about 3 months' age. Compressional wave velocity data are about the same for both plugs. Dynamic modulus data for the second plug are about 50% higher than any previous field or laboratory data at a comparable age of 28 days. At 56 days' age the strength increased by 21%, and the modulus increased by 13% (from the 28-day data). Strength at

TABLE 38
Physical Properties, BCT-1FF

<u>Age (days)</u>	<u>Plug ONE 9/26/79</u>	<u>Plug ONEX 2/14/80</u>
Unconfined compressive strength (psi)		
1	--	4,840
3	--	8,410
7	--	10,610
14	10,870	10,670
21	--	11,350
28	--	11,450
56	13,440	13,850
90	12,750	15,900
Compressional wave velocity (ft/s)		
19	12,945	--
28	--	13,770
56	13,140	13,507
130	13,612	13,785
Dynamic Modulus (E, 10 ⁶ psi)		
19	2.36	3.8
28	--	3.8
56	2.40	4.3
130	2.44	4.6

90 days' age has increased about 15% and the modulus at 130 days has increased by about 9% (from the 56-day data). Additional testing at later ages will include static modulus-of-elasticity measurements during unconfined compression testing to compare with the dynamic modulus determined by resonant frequency.

Density and porosity data for samples of each of the plugs are listed in Table 39. The highest values of porosity are for the SBS specimen which was cast in the field by pouring grout down through brine water standing in the hole in the anhydrite core. Density and porosity data are consistent with the previous laboratory studies of borehole plugging development mixtures.

Expansion data in Table 40 are average values for two or more prisms which are uncoated and inundated in brine water. Initial length and volume datum for each bar was established at about 21 to 25 hours' age when the prism was demolded. A length comparator conforming to ASTM C-490 was used to measure length changes of the restraining rod or small metal bolts embedded in the ends of unrestrained prisms. Volume changes were measured by comparing the weight immersed in water to the weight in air. The 2-inch restrained prisms conform to ASTM C-806-75 and have the most restraint provided by a 1/4-inch threaded steel rod. The 3-inch restrained prisms are restrained by a 3/16-inch threaded steel rod. Therefore, the relative restraint factor is about 4 times greater for the smaller 2-inch prism compared to the 3-inch prism.

Linear expansions for all sizes of restrained and unrestrained prisms are less for the samples from plug ONE (Table 40); however, the same prisms have greater volumetric expansions than those from plug ONEX (with greater linear expansions). All prisms show positive expansions after 7 days' age. One factor that might account for the differing expansions was a higher peak temperature in the curing tank during the first 24 hours in September. The temperature reached at least 160°F before lowering the next morning to about 100°F for the initial data at the time of demolding. The peak temperature was kept to about 120°F for the February ONEX plug by having a larger curing tank and removing the insulation for the first 24 hours. Also

TABLE 39

Density and Porosity

	Dry Density (g/cm ³)	Grain Density (g/cm ³)	Porosity (%)
<u>9/26/79 Plug ONE at 105 Days' Age</u>			
3 x 13 Cylinder, Top	1.878	2.715	30.83
3 x 13 Cylinder, Bottom	1.724	2.668	35.38
Grout from Permeability Specimen			
Top 1	1.908	2.709	29.57
Top 2	1.911	2.860	33.18
Bottom 1	1.910	2.803	31.86
Bottom 2	1.900	2.773	31.48
<u>2/14/80 Plug ONEX at 75 Days' Age</u>			
6 x 12 Cylinder			
Top 1	1.931	2.836	31.91
Top 2	1.964	2.708	27.47
Bottom 1	1.922	2.743	29.93
Bottom 2	1.925	2.790	31.00
6 x 12 Cylinder			
Top 1	1.953	2.775	29.62
Top 2	1.951	2.727	28.46
Bottom 1	1.933	2.770	30.22
Bottom 2	1.934	2.846	32.04
Grout from SBS Specimen			
Top	1.896	2.829	32.98
Middle	1.857	2.814	34.01
Bottom	1.896	2.811	33.51

TABLE 40

Expansion Data
BCT-1FF Field Pours

Bar Size and Restraint (Age)	Linear Expansion (%)		Volumetric Expansion (%)	
	Plug ONE	Plug ONEX	Plug ONE	Plug ONEX
	<u>9/26/79</u>	<u>2 14/80</u>	<u>9/26/79</u>	<u>2/14/80</u>
1-in Unrestrained				
3 days	.010	.271	- .04	.10
7 days	.026	.372	- .25	.22
14 days	.059	.416	.82	.54
28 days	.063	.455	2.01	.29
56 days	.086	.506	2.37	.39
90 days	.098	.530	2.74	.49
2-in Restrained				
3 days	.013	.049	.10	.48
7 days	.006	.086	.42	.51
14 days	.016	.090	.40	.71
28 days	.010	.091	1.20	.38
56 days	.015	.108	1.25	.32
90 days	.024	.117	1.62	.58
2-in Unrestrained				
3 days	.001	.325	.18	.60
7 days	.005	.435	.68	.68
14 days	.022	.446	.72	.97
28 days	.014	.457	1.56	.61
56 days	.018	.484	1.40	.65
90 days	.018	.496	1.71	.75
3-in Restrained				
3 days	- .001	.209	.08	.66
7 days	- .011	.267	.15	.75
14 days	.014	.276	.16	.96

TABLE 40--Continued

Bar Size and Restraint (Age)	Linear Expansion (%)		Volumetric Expansion (%)	
	Plug ONE	Plug ONEX	Plug ONE	Plug ONEX
	<u>9/26/79</u>	<u>2 14/80</u>	<u>9/26/79</u>	<u>2/14/80</u>
3-in Restrained--Continued				
28 days	.001	.268	.70	.52
56 days	.010	.280	1.32	.54
90 days	.010	.292	.78	.55
3-in Unrestrained				
3 days	- .004	.283	- .06	.70
7 days	.004	.386	- .02	.86
14 days	.017	.388	.09	1.03
28 days	- .006	.383	.56	.66
56 days	- .001	.396	1.04	.60
90 days	.001	.410	.86	.95

the temperature of the tank was closely controlled to $\pm 2^{\circ}\text{F}$ in February up to the time of shipment to the lab. Data for both plugs show good positive expansions through 90 days' age.

These values for inundated prisms are upper limits of expansivity and will be monitored particularly for long-term durability under exposure to brine water. Prisms are being cured by two other methods to try to prevent moisture addition and moisture loss. Protection by two layers of a "paint-on" membrane and double layers of plastic bags have not completely prevented moisture loss for samples placed just above the water level or some water addition for submerged protected samples. These data will be included and evaluated in future reports.

The dry samples of cement and fly ash which were taken during batching operations were analyzed for chemical and physical properties. The data are listed and compared to materials from Dowell's bulk plant in February 1979

which were used for the laboratory development work (Tables 41 and 42). The Class H cement data show close agreement for chemical analysis of the three samples. Calculated values of C_3S are greater for the later two samples and probably account for the earlier final setting times. The 7-day strength data are close for the three samples. Data for the three fly-ash samples show greater differences for this material which is a waste product of the combustion process in the power plant source.

During cleaning operations in the AEC-7 hole for the plug ONEX in February, some blackish water and black sludge were removed from just above the top of the hardened plug ONE. This material was examined to determine its composition and any evidence of deterioration of the cement grout plug.

The sample was an oily appearing black liquid sludge. Two portions of this material were filtered and dried. One of the portions was washed first to remove chlorides. Both the washed and unwashed dried material was examined by X-ray diffraction, using an X-ray diffractometer with nickel-filtered copper radiation.

The blackish water filtered from the sample and the sludge that had been filtered, washed, and dried were analyzed chemically. For comparison, a sample of the dry-mixed grout and of a 48-day-old field-cast grout cube were also analyzed.

X-ray diffraction showed that the unwashed dried samples consisted largely of gypsum, anhydrite, halite, and one or more forms of iron. Also present were small amounts of quartz, clay-mica, and 14 Å clay. This composition indicated that the solid parts of the sample came from wall rock in the hole; the gypsum came from hydration of the anhydrite. High iron was indicated by high background in the X-ray pattern, but specific identification was not possible in the presence of so many gypsum peaks. It is likely that the iron was a mixture of metallic iron, magnetite, and perhaps amorphous forms of sulfides, oxides, and hydroxides. Magnetic material was present. The iron probably represents corrosion of tubing and casing by brine water. Additional testing indicated that corrosion of steel was enhanced by the presence of a small amount of H_2S in the brine water.

TABLE 41

Chemical and Physical Properties of Class H* Cement for BCT

	<u>Lab Dev</u>	<u>Plug ONE</u> <u>9/26/79</u>	<u>Plug ONEX</u> <u>2/14/80</u>
WES Sample No.	RC-836	RC-836 (3)	RC-836 (4)
Date Sampled	2/12/79	9/12/79	2/13/80
Fineness (cm ² /g)	2570	2390	2700
C ₃ A (%)	4.8	4.8	3.7
C ₂ S (%)	34	21	23
C ₃ S (%)	43	56	53
C ₄ AF (%)	12	10	12
SiO ₂ (%)	23	22	22
Al ₂ O ₃ (%)	4.3	4.0	4.1
Fe ₂ O ₃ (%)	3.9	3.4	3.8
MgO (%)	2.3	2.3	2.9
SO ₃ (%)	2.2	2.2	2.1
Loss on Ignition (%)	0.5	0.6	0.5
Total Alkalies, as Na ₂ O (%)	0.31	0.51	0.52
Na ₂ O (%)	0.14	0.13	0.13
K ₂ O (%)	0.56	0.57	0.59
Insoluble Residue (%)	0.95	0.20	0.22
CaO (%)	64	64	64
Air Content (%)	9.8	9.7	10.3
7-d Comp. Strength (psi)	2200	2150	2410
Initial Set (hr:min)	3:30	3:10	3:25
Final Set (hr:min)	6:00	5:15	5:30
Sp Gr.	--	3.21	3.23

*Source Dowell Batch Plant, Artesia, NM

Producer--Lone Star Cement Co., Maryneal, TX, Plant

TABLE 42

Chemical and Physical Analysis of Fly Ash for BCT

	<u>Lab Dev</u>	<u>Plug ONE 9/26/79</u>	<u>Plug ONEX 2/14/80</u>
WES Sample No.	AD592	AD592(3)	AD592(4)
Date Sampled	2/12/79	9/25/79	2/12/80
SiO ₂ (%)	39.9	26.7	32.7
Al ₂ O ₃ (%)	21.1	18.5	16.7
Fe ₂ O ₃ (%)	5.3	6.4	6.4
CaO (%)	26.2	38.8	29.9
MgO (%)	3.6	5.0	5.6
SO ₃ (%)	1.5	2.8	2.9
Total Alkalies, as Na ₂ O (%)	1.73	1.29	1.22
Na ₂ O (%)	1.14	--	0.98
K ₂ O (%)	0.89	--	0.36
Loss on Ignition (%)	0.2	0.24	0.4
Fineness (g/cm ²)	3740	4070	--
Specific Gravity	2.63	2.84	2.70
Autoclave Expansion (%)	0.08	-0.06	0.08
Lime-Pozzolan Strength (psi)	1670	990	880

There was no indication of hydrated cement compounds or of unhydrated cement in the X-ray diffraction patterns. The results of the chemical analyses are shown in Table 43. Composition of the dried sludge is in agreement with the compounds which were found by X-ray diffraction.

Comparison with the two grout samples shown in the table also indicates as did the X-ray diffraction, that dissolved portland cement is not present in the sludge. It is concluded that the material removed from the hole is largely loose or dissolved wall rock and corrosion products from the tubing and casing and is not harmful to the cement grout plug with which it is in contact.

TABLE 43

Partial Chemical Analyses of Black Sludge (CL-30 W-5)
from Hole AEC-7 and of Two Grout Samples

Composition (%)	Black Water Filtered from CL-30 W-5	Black Sludge, Filtered, Washed, and Dried (CL-30 W-5) *	Dry-Mixture of Grout Mixture BCT-1-FF	48-day Old Grout Cube (CL-30 Grt-157)†*
SiO ₂	0.0003	7.40	22.31	22.35
CaO	0.15	24.11	52.44	50.18
Fe ₃ O ₄	n.d.‡	19.36	3.83	3.62
SO ₄	n.d.‡	40.86	0.14	7.18
Al ₂ O ₃	0.0001	1.36	7.54	6.40

*Dried to constant weight at 105°C.

† Cast in field February 14, 1980, at time of placement of second grout plug in hole AEC-7. This is grout mixture BCT-1-FF.

‡ Not determined.

References

1. C. W. Gulick, Jr., "Borehole Plugging-Materials Development Program," SAND78-0715 (Albuquerque, NM: Sandia National Laboratories, June 1978).
2. C. L. Christensen and T. O. Hunter, "Waste Isolation Pilot Plant (WIPP), Borehole Plugging Program Description," SAND79-0640 (Albuquerque, NM: Sandia National Laboratories, August 1979).
3. D'Appolonia Consulting Engineers, Inc., "Development of Plan and Approach for Borehole Plugging Field Testing," Report No. ONWI-3 (Prepared for Office of Nuclear Waste Isolation, Columbus, Ohio, October 1978).
4. C. W. Gulick, Jr., "Borehole Plugging Materials Development," Report 2, SAND79-1514 (Albuquerque, NM: Sandia National Laboratories, February 1980).
5. J. A. Boa, Jr., "Borehole Plugging Program (Waste Disposal)," Report 1, "Initial Investigations and Preliminary Data," U.S. Army Engineer Waterways Experiment Station, Miscellaneous Paper 6-78-1, January 1978 (Sandia Report SAND77-7005).
6. "Method of Test for Water Permeability of Concrete," CRD-C 48-78, Handbook for Concrete and Cement, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.
7. A. D. Buck and J. P. Burkes, "Examination of Grout and Rock from Duval Mine, New Mexico," U.S. Army Engineer Waterways Experiment Station, Miscellaneous Paper SL-79-16, July 1979, Vicksburg, Mississippi.
8. American Petroleum Institute Bulletin 10B, "API Recommended Test Practices for Testing Oil-Well Cements and Cement Additives," 1974.
9. D. M. Roy, et al, "Borehole Cement and Rock Properties Study, Task I. Borehole Plugging Cement Studies," Annual Progress October 1, 1978-September 30, 1979, ONWI/SUB/78/E512-00500-4, Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania, 11/30/79.
10. M. W. Grutzeck, et al, "Modified Cement-Based Borehole Plugging Materials: Properties and Potential Longevity," [Paper presented at OCED/ONWI Workshop on Borehole and Shaft Plugging, Columbus, Ohio (7-9 May 1980)], Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania.
11. D. M. Roy, "Geochemical Factors in Borehole and Shaft Plugging Materials Stability," [Paper presented at OCED/ONWI Workshop on Borehole and Shaft Plugging, Columbus, Ohio (7-9 May 1980)], Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania.

12. J. G. Moore, et al, "Cement Technology for Plugging Boreholes in Radioactive Waste Repository Sites: Progress Report for the Period October 1, 1978, to September 30, 1979; ORNL 5610, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.
13. E. W. McDaniel, "Cement Technology for Borehole Plugging: An Interim Report on Permeability Measurements for Cementitious Solids," ORNL/TM-7092, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, January 1980.
14. R. D. Statler, "Bell Canyon Test--Field Preparation and Operations," SAND-0458C, prepared for the International Borehole Plugging Symposium, Columbus, Ohio, May 1980 (Albuquerque, NM: Sandia National Laboratories).

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