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Borehole Plugging Materials Development Program Report 2

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SF 2900 Q(7-73)

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SAND79-1514
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Printed February 1980

ONWI/SNB/79
E511-03700-MDR-1

BOREHOLE PLUGGING MATERIALS DEVELOPMENT PROGRAM REPORT 2

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ABSTRACT

The data for 2 yr of grout mixtures durability studies developed for the borehole plugging program of the Nuclear Waste Isolation Pilot Plant (WIPP) are reported. In addition, data for 1 yr of durability studies of grout mixture field samples used to plug the ERDA No. 10 exploratory drill hole near the WIPP site are included. The grout samples and the data do not show any evidence of deterioration during the durability studies that include exposure to brine at both ambient and elevated temperatures. The data include strength, compressional wave velocity, dynamic modulus, expansion, weight change, porosity, permeability, bond strength, chemical analysis of cements, and petrographic examinations. The work was performed at the Concrete Division of the Structures Laboratory of the US Army Engineer Waterways Experiments Station (WES), Vicksburg, Mississippi. The work is continuing at WES.

ACKNOWLEDGMENT

This report was prepared jointly by Sandia Laboratories and the US Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi. The studies were conducted at the WES Concrete Division, Structures Laboratory, under the direction of B. Mather, J. M. Scanlon, R. A. Bendinelli, and J. A. Boa, Jr. D. M. Walley was in charge of field activities for plugging the ERDA No. 10 drill hole and supervised handling and testing of all samples and cores from the field. A. D. Buck performed the x-ray diffraction and scanning electron microscope studies and evaluations. C. W. Gulick coordinated the study program and evaluation of data.

Funding for the program was provided to Sandia by the Department of Energy through the Office of Nuclear Waste Isolation at Battelle Memorial Institute. Sandia provided the funding to WES.

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1. INTRODUCTION AND BACKGROUND

Development studies of cementing materials for the Borehole Plugging Program have been underway at the US Army Engineer Waterways Experiment Station (WES) Structures Laboratory since June 1975. Sandia's Waste Management Technology Department has technical responsibility for the studies. The initial investigations and preliminary data for the study and development program are reportd and discussed in References 1 and 2. The studies focus on achieving durability of borehole plugs by choice of cement, addition of flyash, reducing the water/cement ratio while maintaining pumpability.

This report includes the data derived from 2 yr of aging the samples of five laboratory mixtures. The sources of the grout materials and the laboratory testing procedures are listed and discussed in Reference 1. The formulation of the brine solution in which specimens are inundated is listed in Table 10 (Reference 1). The brine solution is similar to samples of underground waters at the Waste Isolation Pilot Plant (WIPP) site.

The reasons for selecting the El Toro ChemComp brand of Type K expansive cement are listed in Reference 2. The following discussion reviews some of the features of an expansive cement. The general definition for expansive cement is a cement which when mixed with water forms a paste that after setting increases in volume to a significantly greater degree than portland cement paste.[3] The source of the expansive force is generally recognized as the formation of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$). The expansive potential of the cement and the effective modulus of elasticity of the wall rock of the borehole at the location of the plug control the expansion in the plug. For one of the study grout mixtures, a Type K self-stressing cement was included to study the effect of a greater expansive potential.

Because of the general shortage of portland cement, the El Toro ChemComp cement and the Type K self-stress cement are not currently being manufactured. The durability of these cements is considered good and the higher level of expansion to tighten a plug at the rock interface is desirable; future availability is unknown. The existing specimens of the four laboratory mixtures using these cements will continue to be monitored and evaluated.

Because of the unavailability of these expansive cements, additional proportioning studies were undertaken. The cements selected were API Class C with high-sulfate resistance and the coarser API Class H cement that has a lower water demand. The results of these proportioning studies are included in Section 2.

In 1977 the decision to plug the exploratory drill hole ERDA No. 10 near the WIPP site provided an opportunity to start a quality control and quality assurance program for hole plugging under field conditions. The entire batching and mixing operations were under the close supervision of WES staff members. The description of field activities related to the plugging operations are reported in Reference 3.

During the plugging operations of ERDA No. 10, a number of samples were obtained and shipped to WES for testing and inclusion in the long-term durability exposure studies. Included were samples of each material in the mixture, dry samples of blended materials from bulk trucks both at the plant and at the field site, cylinder specimens molded during the mixing and pumping of each of the plugs, cores drilled from Plug No. 1 after hardening, and samples of recirculated grout returns from Plug No. 3. Test data from these samples are included in Section 3. All of the data to date show a good quality for the grout mixtures actually placed in the field.

2. LABORATORY MIXTURE INVESTIGATION

2.1 Long-Term Durability Studies

The basis for selecting the five grout mixtures for the long-term durability studies is given in References 1 and 2. The mixture proportions are listed in Table 2-1. The samples were molded between August 1976 and February 1977. After curing for 28 days (d), the samples listed as inundated were immersed in a tank of water that simulated the ground water at the WIPP site. A footnote to Table 8 of Reference 1 lists the chemical formulation of the water used until October 1978. The water was replaced by the formulation listed in Table 10 of Reference 1 which has been used for inundating specimens since October 1978 and will continue to be used. The temperature of the water for these studies is about 75° ± 5°F.

Samples that are not inundated in the brine solutions have been coated with paint-on plastic and stored in double plastic bags. From these and other studies, it is apparent that there is some moisture loss over extended periods of time with this method.

The compressional wave velocity and dynamic modulus data in Table 2-2 confirm visual observations that no deterioration of samples has occurred through 2 yr of aging. The variations are random and are within the range of accuracy of the meaurement technique for the size of specimen.

The push-out bond strengths (against black iron pipe) are shown through 1-yr age in Table 2-3. The two mixtures with brine mixing water (Nos. 2 and 5) have a significant increase in bond strength during the period of 180 d to 1 yr. Mixtures containing salt apparently have a higher bond strength, perhaps due to corrosion of steel.

A block of halite from the WIPP site was made available for the development studies. Mixtures 2 and 5 were tested for bonding by casting a 2-in. annulus of grout around a 4-in.-dia halite core. At 28-d age, the push-out bond strength was 710 psi for Mixture 2 and 865 psi for Mixture 5. This value for Mixture 2 is comparable to the 28-d data in Table 2-3. The value for Mixture 5 is significantly above all values through 2-yr age for bonding to pipe.

The unrestrained length change data of 3 x 3 x 10-in. prisms in Table 2-4 shows that all specimens have small and stable length changes through 2 yr of age. The data are plotted in Figures 2-1 through 2-5. The specimens in plastic-bag storage show the moisture loss by length reductions of -0.160% to -0.226% for all five mixtures. The inundated prisms show increases of 0.047% to 0.135% for all except Mixture 4 which contains additional pozzolan. This mixture maintains its approximate initial length (at 28-d age). The maximum expansion of 0.135% occurred for Mixture 2 which combines the shrinkage-compensated expansive cement with brine mixing water. Data on change in mass for the inundated bars is listed in Table 2-5. This data also confirms the stability and lack of deterioration of Mixture 2. Mixture 2 also has the greatest increase in mass (2.6%) and shows a steadily decreasing rate of increase in mass (0.5% for the second year).

The density data in Table 2-6 and the porosity data in Table 2-7 were determined on NX-size cores from the original 6 x 12-in. cast cylinders. The core plugs were approximately 2-1/8 in. dia by 4 in. in length. The plugs were dried to constant mass at 140°F to prevent any test-induced change in the matrix of hydration products. The results in the two tables for bulk solid density and porosity were then determined by the pressure pycnometer method (all but the final column in each table for noninundated specimens). The pycnometer method subjected the specimens to 1200-psi water pressure and the bulk solid density and porosity were calculated from the increase in weight. The data in the final column was determined by crushing the specimen to pass the 600-μm (30 mesh) sieve to determine the bulk solid density and then calculate the porosity.

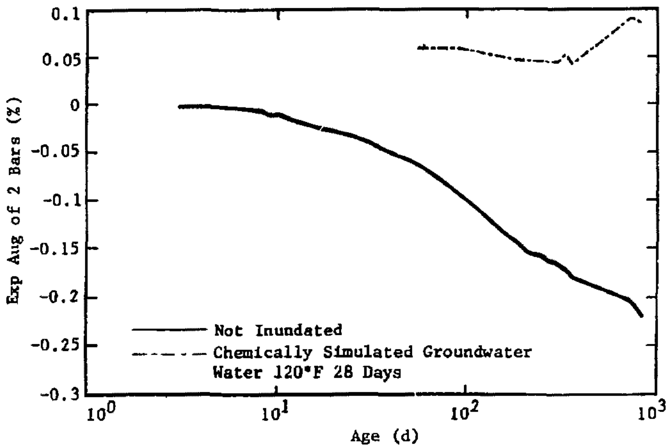

Figure 2-1. Expansion Data for Mixture BPN-FA-SP-P Unrestrained Bars

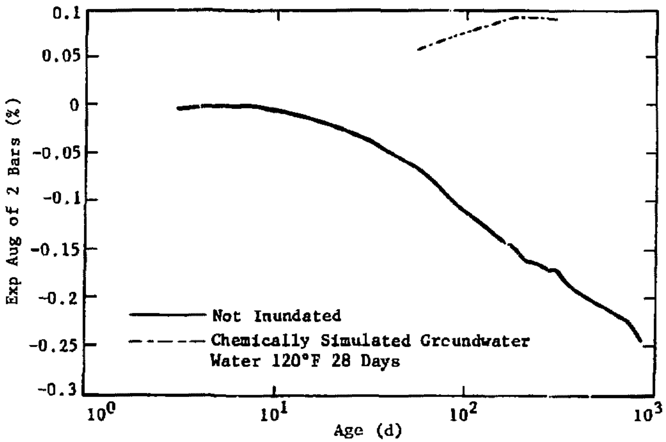

Figure 2-2. Expansion Data for Mixture BPN-FA-BS-SP-P-1 Unrestrained Bars

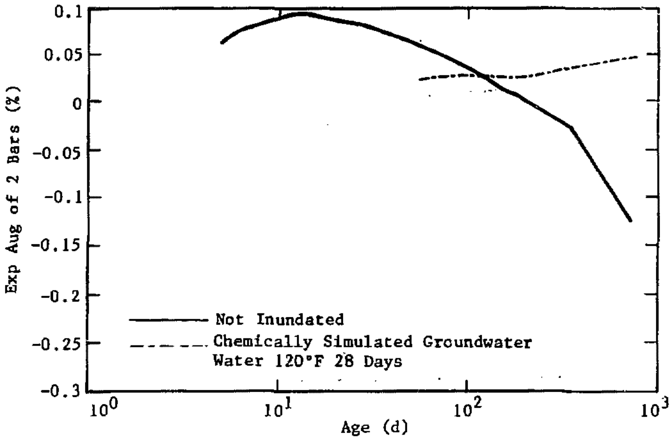

Figure 2-3. Expansion Data for Mixture BPN-CS-FA-1 Unrestrained Bars

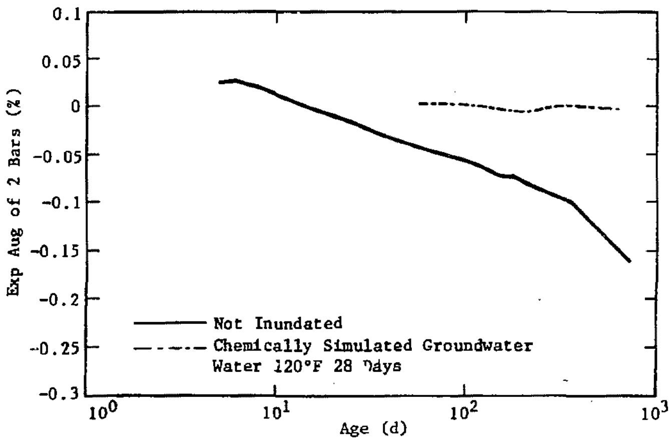

Figure 2-4. Expansion Data for Mixture BP-521-25MP Unrestrained Bars

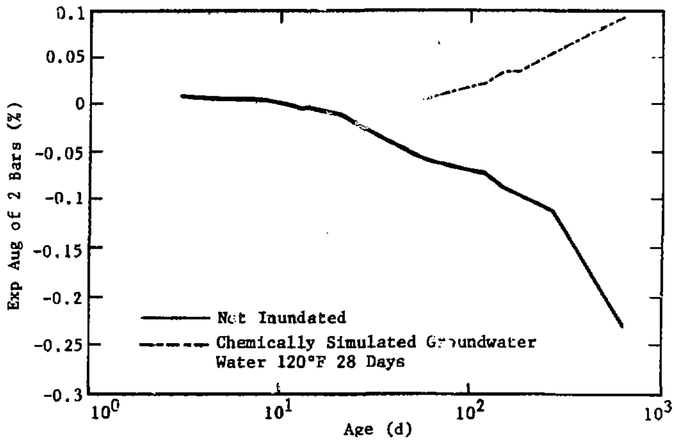

Figure 2-5. Expansion Data for Mixture BPN-FA-BS-SP-P-1 (Type III) Unrestrained Bars

The trend most evident is the increase in bulk solid density for the two mixtures with brine mixing water (Nos. 2 and 5). The increase is about 17% to 22%. The porosity data for Mixture 5 show a maximum value at 1 yr and then a decrease at 2 yr. The data for the other three mixtures with fresh mixing water are random without a clearly defined trend. The significance is not understood at this time. Future data on the samples at later ages may establish the significance of the variations.

Water permeability measurements were made by CRD-C 48-73,[4] Method of Test for Water Permeability of Concrete. The test consisted of subjecting specially prepared 6-in.-dia specimens to 200-psi water pressure (using the simulated WIPP groundwater). For specimens tested at an age of about 1 mo, only Mixture 5 exhibited any flow of water through the specimen. The data in Table 2-8 are for Mixture 5 at 18- to 30-d age. The data were pre-sented in Tables 7 of Reference 1; however the values in microdarcies were incorrect due to an incorrect conversion factor. The corrected data are shown in Table 2-8. The test was performed on specimens at 2-yr age; the data is listed in Table 2-9. The test of the Mixture 4 specimen did not give useful data. The water-permeability values are all less than 1 μD.

Additional testing for gas permeability and porosity was done by a commercial laboratory. The procedures followed were standard for rock cores. Drying was accomplished at 200°F for 4 h and 300°F for 12 h. These temperatures may be too severe for the high water-content grout specimens and may alter the hydration product matrix in addition to driving off the normal evaporable water. The results are listed in Table 2-10. Gas permeability values are significantly higher than the water permeability values in Tables 2-8 and 2-9. The permeability of the three mixtures made using fresh mixing water (1, 3, 4) was more than 3 orders of magnitude higher than that of specimens from mixtures made using brine as mixing water. The drying temperatures may have some influence.

The method for determining porosity used air at a pressure differential of 30 mm of mercury. All values are lower than comparable values determined at WES. The data in the last two columns of Table 2-10 are closer to the WES values. These samples were cored from specimens which have been tested at WES by forcing water into the void structure at 1200 psi. The data for all the samples with brine mixing water (Mixtures 2 and 5) show very low porosities of less than 7% except for the actual specimens previously tested at WES. The low differential pressure may account for the low values that are not considered valid for grouts.

2.2 Additional Proportioning Studies

The basic shrinkage-compensated expansive cement with high sulfate resistance is not currently available. For this reason additional proportioning studies were undertaken using API Class C cement with high sulfate resistance and the coarser API Class H cements. The basic approach was to start with proportions similar to laboratory Mixture 2 (BPN-FA-BS-SP-P-1)[1 2] and then to achieve maximum density while retaining adequate flow for 3 h.

The mixture proportions and flow data are listed in Table 2-11. The Class H cement from Southwestern Portland Cement Company, El Paso, Texas, was selected because of the coarseness of the cement, low water demand, and high sulfate resistance. By using the superplasticer Melment L-10, a density of 130.1 lb/ft^3 was achieved for mixture 6H-3. The Class C (SR) cement from Lone Star Industries, Maryneal, Texas, was selected for study because of the low C_3A content that ensures a high level of sulfate resistance. The highest density achieved for this fine cement was 125.1 lb/ft^3 (mixture 6C-1) which is greater than any previous laboratory study mixtures (but less than the 6H-2 and 6H-3 mixtures).

The flow measurements used the flow-cone method (CRD-C79-77).[4] All mixtures maintained adequate workability for more than 3 h by mixing for 3 min every 15 min to simulate requirements during field-cementing operations.

TABLE 2-1

Grout Mixture Proportions

Constituent	Unit	1. BPN-FA-SP-P	2. BPN-FA-BS-SP-P-1	3. BPN-CS-FA-1	4. BP-521-25MP	5. BPN-FA-BS-SP-P-1 (Ty III)
Cement, Type III	lb/ft^3					55.21
El Toro Chem Comp	lb/ft^3	61.12	55.21	62.02	43.54	-
ChemStress	lb/ft^3	-	-	9.00	9.00	
Flyash	lb/ft^3	20.56	18.58	16.76	12.40	18.58
Tufa (pozzolan)	lb/ft^3	-	-	-	9.84	
Fine Salt (dissolved)	lb/ft^3	-	11.43	-	-	11.43
Melment L10	lb/ft^3	1.63	1.48	1.73	2.10	1.48
Plastiment	oz/ft^3	2.60	2.94	3.02	2.76	2.94
Water	lb/ft^3	34.31	31.73	32.66	36.14	31.73
w/c+pozz	wt	0.42	0.43	0.37	0.48	0.43

TABLE 2-2

Dynamic Modulus and Compressional Wave Velocity

Test	Specimen Age	Specimen Condition	Mixture 1 BNP-FA-SP-P	Mixture 2 FA-BS-SP-P-1	Mixture 3 BPN-CS-FA-1	Mixture 4 B-521-25MP	Mixture 5 BPN-FA-BS-SP-P-1 (Type III)
Dynamic Modulus ($psi \times 10^6$)	28-d		2.36	1.94	3.39	2.30	2.10
	56-d	Wet	2.91	2.09	3.35	2.37	2.30
		Dry			3.20	2.30	2.20
	90-d	Wet	2.79	2.02	3.43	2.34	2.25
		Dry	2.32	1.83	3.31	2.44	2.05
	180-d	Wet	2.83	2.00	3.36	2.33	2.29
		Dry	2.00	1.95	3.32	2.40	2.12
	1-yr	Wet	2.74	2.17	3.50	2.45	2.36
		Dry	2.48	2.21	3.44	2.20	2.10
	2-yr	Wet	2.47	2.27	3.59	2.52	2.33
		Dry	2.70	2.30	3.00	2.20	2.23
Compressional Wave Velocity (ft/s)	28-d		11,465	10,430	12,860	11,300	10,860
	56-d	Wet	11,220	10,360	12,440	10,875	11,220
		Dry			12,345	10,970	11,245
	90-d	Wet	12,085	10,700	12,500	11,155	10,590
		Dry	11,855	10,570	12,675	11,405	11,190
	180-d	Wet	11,590	10,340	13,435	11,730	10,225
		Dry	11,110	10,430	13,305	11,615	10,350
	1-yr	Wet	11,825	10,825	12,800	11,215	11,165
		Dry	11,365	10,635	12,700	11,265	11,030
	2-yr	Wet	11,520	11,315	12,980	11,335	11,415
		Dry	11,110	10,860	12,210	11,360	11,145

NOTE: Specimens were cured 0-28 d at 120°F.
Results shown "wet" indicate specimens were stored in specially prepared water to simulate groundwater from a site near Carlsbad, NM.

The 28-d results are on specimens prior to inundation. All results listed as wet were of specimens continuously inundated from 28-d age on.

TABLE 2-3

Bond Strength

Mixture	Results (psi) at Ages Shown*				
	28-d	56-d	90-d	180-d	1-yr
BPN-FA-SP-P	710 (80,000)	655 (73,750)	--	430 (48,250)	500 (56,500)
BPN-FA-BS-SP-P-1	740 (83,500)	605 (68,500)	--	560 (63,000)	855 (96,650)
BPN-CS-FA-1	575 (65,000)	505 (57,000)	465 (52,500)	435 (49,250)	†
BP-521-25MP	365 (40,750)	355 (39,750)	565** (64,000)	250 (28,000)	†
BPN-FA-BS-SP-P-1 (Type III)	420 (47,500)	325 (36,750)	330 (37,000)	480 (54,250)	645 (72,910)

Note: Specimens were cast vertically in smooth-bore, 6-in.-ID black iron pipe. Specimens 6 in. long were cut from opposite ends of the pipe at test ages shown. The bonded area was 113 in.^{2}

This test is intended to indicate whether there is any loss in bond effectiveness with time. These specimens were cast and cured at ambient laboratory conditions (~70°F) in a smooth-wall, steel pipe and therefore represent the worst condition; any roughness in an actual hole or casing would increase bond strength.

* Load (in lbf) to break bond is shown in parentheses. Load is an average of two tests.

** This value is probably not representative.

† No specimens available for testing.

TABLE 2-4

Length Change (3 x 3 x 10-in. Prisms, %)

Age	BPN-FA-SF-P		BPN-FA-BS-SP-P-1		BPN-CS-FA-1		BP-521-25MP		BPN-FA-BS-SF-P-1 (Type III)	
	Percent*	Percent**	Percent*	Percent**	Percent*	Percent**	Percent*	Percent**	Percent*	Percent**
2 d	Initial reading		Initial reading		Initial reading		Initial reading		Initial reading	
3 d	-0.003		-0.005						0.007	
4 d	-0.002		-0.003							
5 d					0.062		0.024			
6 d					0.074		0.026		0.004	
7 d	-0.005		-0.002						0.004	
8 d	-0.007		-0.003		0.084		0.019		0.003	
9 d	-0.010		-0.006						0.001	
10 d	-0.011		-0.007						0.000	
11 d	-0.015		-0.009							
12 d					0.094		0.004			
13 d									-0.006	
14 d	-0.021		0.014		0.094		-0.001		-0.005	
21 d	-0.030		-0.024		0.087		-0.012		-0.012	
28 d	-0.037	Initial reading	-0.033	Initial reading	0.082	Initial reading	-0.022	Initial reading	-0.026	Initial reading
56 d	-0.063	0.059	-0.66	0.057	0.038	0.022	-0.043	0.002	-0.057	0.003
3 mo	-0.92	0.059	-0.104	0.074	0.040	0.027	-0.054	0.002	-0.067	0.015
4 mo	-0.113		-0.123		0.026		-0.064		-0.072	
5 mo	-0.130		-0.139		0.013		-0.072		-0.088	0.034
6 mo	-0.142	0.047	-0.148	0.093	0.007	0.025	-0.074	-0.005	-0.095	0.034
7 mo	-0.154		-0.0162							
8 mo	-0.157		-0.165							
9 mo	-0.163	-0.171							-0.111	0.054
10 mo	-0.0165	0.045	-0.170	0.092						
11 mo	-0.171	0.053	-0.180	0.104						
12 mo	-0.178	0.043	-0.187	0.099	-0.028	0.036	-0.100	-0.002	-0.151	0.067
2 yr	-0.203	0.092	-0.226	0.135	-0.125	0.047	-0.160	-0.003	-0.231	0.093

NOTES:

* Specimens in the first column under each mixture were cast and cured at ambient laboratory conditions (~70°F). Even though coated with a protective paint-on skin and stored in double plastic bags, some drying occurred, thereby causing shrinkage.

** Specimens in the second column under each mixture were cured from 1 to 28 d at 120°F to more closely simulate actual downhole conditions. They were not demolded until 28-d age, at which time they were read and inundated in the laboratory-simulated ground water to be read at ages shown.

TABLE 2-5

Weight Change Data (grams)

Mixture		28 d	56 d	180 d	1 Yr	2 Yr	Gain 28 to 56 d	Gain 56 to 180 d	Gain 180 d to 1 Yr	Gain 1 yr to 2 Yr	Gain 56 d to 2 yr (gm)	Gain 56 d to 2 yr (%)
BPN-FA-SP-P	1	3936	4215	4259	4276	4290	315	6	17	14	75	1.8
	2	3870	4153	4154	4173	4184	273	11	19	11	31	0.7
	3	3893	4062	4089	4110	4126	169	27	21	16	64	1.6
BPN-FA-BS-SP-P-1	1	3995	4059	4112	4150	4169	64	53	38	19	110	2.7
	2	4112	4178	4230	4266	4286	66	52	36	20	108	2.6
	3	4060	4124	4176	4212	4232	64	52	36	20	108	2.6
BPN-CS-FA-1	1	4415	4452	4467	4482	4492	37	15	15	10	40	0.9
	2	4364	4390	4409	4423	4443	26	19	14	20	53	1.2
	3	4313	4346	4363	4379	4390	33	17	16	11	44	1.0
BP-521-25MP	1	4065	4076	4071	4075	4082	11	-5	4	7	6	0.1
	2	4010	4017	4006	4008	4013	7	-11	2	5	-4	-0.1
	3	4023	4034	4031	4033	4039	11	-3	2	6	5	0.1
BPN-FA-BS-SP-P-1 (Type III)	1	4315	4339	4356	4363	4365	24	17	7	2	26	0.6
	2	4315	4340	4355	4363	4365	25	15	8	2	25	0.6

NOTE: Weight changes of 3 x 3 x 10-in. prisms inundated at 28-d age and used for unrestrained length change measurements.

TABLE 2-6

Density (g/cm^2)

Specimens	28 d Oven Dry	28 d Bulk Solid	56 d Oven Dry	56 d Bulk Solid	180 d Oven Dry	180 d Bulk Solid	1 Yr Oven Dry	1 Yr Bulk Solid	2 Yr Oven Dry	2 Yr Bulk Solid	2 Yr Crushed Oven Dry	2 Yr Crushed Bulk Solid
Noninundated												
BPN-FA-SP-P	1.54	2.56	1.76	2.64	1.56	2.46	1.56	2.45	1.60	2.49	1.70	2.58
	1.53	2.52	1.73	2.39	1.59	2.49	1.57	2.57	1.59	2.49		
BPN-FA-BS-SP-P-1	1.67	2.16	1.64	2.27	1.71	2.22	1.63	2.38	1.55	2.63	1.70	2.58
	1.66	2.22	1.66	2.44	1.77	2.21	1.64	2.43	1.56	2.56		
BPN-CS-FA-1			1.71	2.46	1.66	2.42	1.72	2.46	1.67	2.49	1.74	2.58
			1.70	2.44	1.66	2.43	1.68	2.49	1.67	2.50		
BP-521-25MP			1.44	2.42	1.41	2.46	1.40	2.58	1.40	2.54	1.52	2.4
			1.46	2.39	1.44	2.46	1.43	2.63	1.43	2.46		
BPN-FA-BS-SP-P-1 (Type III)	1.74	2.08	1.61	2.26	1.73	2.04	1.52	2.53	1.72	2.30	1.75	2.57
	1.75	2.07	1.67	2.25	1.70	2.16	1.53	2.54	1.73	2.19		
Inundated												
BPN-FA-SP-P							1.61	2.58	*1.52	*2.69	(20 mo)	
							1.58	2.67				
BPN-FA-BS-SP-P-1							1.67	2.32	*1.50	*2.73	(20 mo)	
							1.66	2.32				
BPN-CS-FA-1									*1.59	*2.61	(16 mo)	
BP-521-25MP									*1.39	*2.64	(16 mo)	
BPN-FA-BS-SP-P-1 (Type III)							1.54	2.63	*1.37	*2.64	(14 mo)	
							1.53	2.53				

*Total Time Inundated.

TABLE 2-7

Porosity (%)

Specimens Mix No. and Designation	28 d	56 d	180 d	1 Yr	2 Yr	2 Yr (Crushed)
Noninundated						
BPN-FA-SP-P	39.3	33.3	36.5	36.2	41.0	34.1
	39.1	27.7	36.2	33.9	39.2	
BPN-FA-BS-SP-P-1	22.0	27.6	22.8	31.5	35.7	34.1
	25.3	31.9	22.7	32.6	35.8	
BPN-CS-FA-1		30.5	31.7	30.0	32.9	32.6
		30.5	31.5	32.6	33.2	
BP-521-25MP		40.6	42.3	45.5	44.9	38.7
		38.8	41.5	45.7	41.9	
BPN-FA-BS-SP-P-1	16.4	26.1	17.8	40.0	29.0	31.9
(Type III)	15.4	25.8	21.0	39.9	21.0	
Inundated						
BPN-FA-SP-P1				*37.7	*43.5	(20 mo)
				*40.7		
BPN-FA-BS-SP-P-1				*30.2	*45.0	(20 mo)
				*28.5		
BPN-CS-FA-1					*39.1	(16 mo)
BP-521-25MP					*47.4	(16 mo)
BPN-FA-BS-SP-P-1				*41.5	*48.1	(14 mo)
(Type III)				*39.5		

*Total Time Inundated.

TABLE 2-8

Water Permeability Mixture
BPN-FA-BS-SP-P-1 (Type III)

(Corrected microdarcy values for Table 7 in Reference 1)

Time Frame (days)	Permeability, $ft^3/s/ft^2$ (ft head/ft length) x 10^{-12}, *Microdarcies (μD) Shown in ( )			
	No. 1	No. 2	No. 3	No. 4
18-22	45.28 (1.43)	21.27 (0.67)	21.57 (0.67)	5.25 (0.16)
26-30	38.73 (1.22)	15.27 (0.48)	16.37 (0.51)	5.46 (0.16)

NOTE: The mixture described above is the only one in which the simulated groundwater permeated the specimen under 200-psi pressure. The other mixtures were impermeable to simulated groundwater and, in some cases, to tap water also. Note that this mixture does not contain any expansive cement.

In addition, specimens of 3-in. length were also tested for permeability and none of these specimens exhibited any permeability under the 200-psi water pressure. The 3-in.-long specimens did not include the mixture described above, but were composed of the four mixtures that were not permeable.

* D = 3.17496 x 10^{-5} $ft^3/(s)\ (ft^2)$ (ft water/ft).

TABLE 2-9

Water Permeability for 2-Yr Old Specimens

Mixture No.	Designation	Specimen No.	Water Permeability Microdarcies (μD)
1	BPN-FA-SP-P	1	0.10
2	BPN-FA-BS-SP-P-1	1	0.16
2	BPN-FA-BS-SP-P-1	2	0.84
3	BPN-CS-FA-1	1	0.13
5	BPN-FA-BS-SP-P-1 (Type III)	1	0.57
5	BPN-FA-BS-SP-P-1 (Type III)	2	0.46

NOTE: All specimens 6-in. diameter by 6-in. length

TABLE 2-10

Gas Permeability and Porosity

Mixture	Age No.	Permeability,[a] Microdarcies (μD) Vertical[c]	Horizontal[c]	Porosity, Percent (%)[b] Inundated Vertical[c]	Horizontal[c]	Vertical[d]	Noninundated Vertical[d]
BPN-FA-SP-P	19	460	90	26.8	28.9	30.0	25.0
		210	760	30.0	28.7	32.9	27.3
BPN-FA-BS-SP-P-1	19	0	20	6.4	6.3	36.3	10.7
		40	340	6.2	5.4	35.1	4.0
BPN-CS-FA-1	15	1210	1530	26.9	28.0	28.1	28.2
		1220	1440	27.3	27.4	29.5	25.6
BP-521-25MP	15	1000	1030	35.2	37.0	37.5	28.2
		1140	1440	32.9	38.4	37.9	27.4
BPN-FA-BS-SP-P-1 (Type III)	12	120	Trace	5.5	3.7	36.8	--
		50	Trace	5.0	5.2	33.3	—

NOTES:

General: All sample plugs were 1-in-dia by 2-in-long cylinders drilled with air. Both the permeability test and the porosity tests were made on the same plug for the same sample.

a. Permeability test was made using the soap-bubble method that measures the flow of air through the sample by movement of a soap bubble in a pipette on the downstream side using an upstream pressure of 300 mm of mercury.

b. Bulk volume was measured in cubic centimeters on each dried sample; then, using the Washburn-Bunting method, a 30-in. vacuum was pulled on the sample. To extract the air filling the pore space, this air volume was then moved to the top of the porosimeter where it was measured directly in cubic centimeters. The pore space divided by bulk volume = porosity.

c. The 1- by 2-in. plug sample cylinders were cored from the side (horizontal) and bottom (vertical) of a 6- by 12-in. cast cylinder which had been inundated in the simulated WIPP site groundwater.

d. These 1- by 2-in. plug samples were cored from NX size cores previously tested for porosity by the pressure pycnometer method at WES.

TABLE 2-11

Grout Mixture Proportioning
Laboratory Mixture 6 (BPN-FA-BS-SP-P-2)

Material*	Unit of Measure	6H	6H-1	6H-2	6H-3	6C	6C-1
Class H Cement	lb/ft^3	59.92	64.78	64.78	70.51	-	-
Class C Cement	lb/ft^3	-	-	-	-	59.76	64.60
Flyash	lb/ft^3	20.17	21.80	21.80	23.73	20.11	21.74
Fine Salt	lb/ft^3	10.96	10.29	10.29	9.50	10.93	10.26
Melment L-10	lb/ft^3	1.61	1.74	3.46	5.66	3.19	5.18
Plastiment	oz/ft^3	1.91	2.07	2.07	2.25	1.91	2.06
Water	lb/ft^3	30.43	28.57	28.57	26.38	30.35	28.49
Density	lb/ft^3	121.5	125.5	125.5	130.1	121.2	125.1
Density	lb/gal	16.2	16.8	16.8	17.4	16.2	16.7
Cement Factor							
Cement	lb/yd^3	1618	1749	1749	1904	1614	1744
Cement + Flyash	lb/yd^3	2162	2338	2338	2544	2156	2331
Water/Cement Ratio							
Cement	-	0.51	0.44	0.44	0.37	0.51	0.44
Cement + Flyash	-	0.38	0.33	0.33	0.28	0.38	0.33
Flow at +5 min	s	13.2	19.8	15.4	18.3	11.0	14.0
Flow at +1 hr	s	15.6	19.4	17.6	18.6	15.0	22.4
Flow at +2 hr	s	14.2	17.4	16.1	18.0	15.6	23.8
Flow at +3 hr	s	14.2	18.2	15.8	18.0	14.8	21.2
Flow at +3 hr	s	-	-	15.4	18.6	-	-

*Intermittent mixing - 3 min mixing; 12 min at rest

3. LABORATORY STUDIES OF ERDA NO. 10 FIELD SAMPLES

3.1 General

Samples obtained from the cementing operation of ERDA 10 exploratory hole have been added to the study program in the laboratory to gain durability data on field cast and cored specimens. The plugging operation and details of the grout mixtures are reported in Reference 3. Members of the staff of WES supervised the batching and mixing, and prepared the cast samples.

The general basis for the three grout mixtures (for the four plugs) was reached during meetings with personnel from Sandia, WES, Fenix & Scisson, and the cementing contractor. The grout-mixture data is listed in Table 3-1. The basis was 30% Litepoz 3 (flyash)/70% Class C (SR) cement. The cement with a zero C_3A content was produced by Lone Star Cement Co. at Maryneal, Texas and is recommended for the severe downhole environment of the Southwest. A fine granulated salt (NaCl) was added for Plugs 1, 2, and 3 that would be placed against the salt formation rock. For Plugs 2 and 3, a fully saturated brine mixing water resulted from 36% salt by weight of water. The salt content was reduced to 30% for Plug 1 to improve strength while still maintaining adequate bonding to the rock. Fresh mixing water was used for the top Plug 4 inside the casing for maximum strength and to prevent chloride corrosion of the steel. Additives for Plug 1, 2, and 3 were calcium chloride (2%), salt gel (attapulgite, 2%), and dispersant (0.1%); were all expressed as percentages by weight of cement plus flyash. Silica sand (5%) was included in the first three plug mixtures to improve strength characteristics and to reduce circulation loss to the formation. The additives for Plug 4 were 2% Bentonite gel and a fresh water turbulent-inducer compound (friction reducer). The physical property data for the mixtures in Table 3-1 were supplied by Dowell. The slurries were tested at the Midland Lab for thickening time and strength gain in accordance with API10B;[5] these tests simulated the downhole environment.

Samples of the individual dry grouting materials used at the batch plant were obtained. Further samples of the dry blended materials were obtained from each material in the bulk trucks before and after transport to the site (about 60-mi distance). Samples of the mixed grout were molded in 6- x 12-in. and 3- x 6-in. cardboard cylinder molds after mixing operations were completed. In addition, six 6- x 12-in. cylinders were filled with grout return from Plug 3 which had been circulated from the hole. Approximately 57 ft of 4-in.-dia core from the top of Plug 1 were obtained after curing in the hole for about 48 h.

All of the samples were allowed to harden at the site for about 24 h and then were transported to the Sandia office in Carlsbad for storage prior to shipment to WES. Some specimens were shipped by air after a minimum of 7-d age; the balance were shipped by surface transportation after 14-d age.

Upon receipt at WES, the surface-cast specimens, cores from Plug 1, and recirculated returns from the top of Plug 3 were selectively tested at varying ages and curing conditions. Tests and studies have included:

Scanning Electron Microscopy (SEM)
X-ray Pattern Analysis
Air Void Content
Compressional Wave Velocity (Vp)
Dynamic Modulus of Elasticity (E_{Dyn})
Porosity and Moisture Content
Water Permeability
Density and Bulk Specific Gravity
Unconfined Compressive Strength

The studies and tests performed during the first year of the aging of specimens were used to develop baseline data for future plugging activities. The cores from the top of Plug 1 were cured in situ for about 48 h before the coring operations commenced. They were subjected to fluid pressure of about 2000 psi from the drilling mud in the hole and 128°F formation temperature. The surface-cast specimens were cured under ambient air temperatures and atmospheric pressure. The air temperatures at the site ranged from a high of 98°F on the afternoon after Plug 1 was completed to a low of about 50°F when Plug 4 was pumped. After the first 24 h of curing, all samples were then placed in a controlled temperature of about 70°F until shipment to WES. The other type of sample available for study was the recirculated return from the top of plugs. This grout had been pumped downhole to the 2313-ft depth and then forced upward in the hole to above the 805-ft depth. When the grout was completely pumped down the tubing, drilling mud was pumped down the annulus forcing the grout above the 805-ft depth up the tubing to the surface where the samples were obtained. This operation subjected these samples to varying and undefined pressures during 1 h of mixing and 2 h of pumping.

3.2 Curing Conditions During Storage

The specific curing condition for each specimen is listed in the data tables in Appendix A. Samples and cores except those destructively tested remained sealed in their containers until 28-d age. At 28-d, all surface cast samples for Plugs 1 and 2 were inundated in tanks of saturated brine at 128°F (3.1 lb of salt (NaCl) per gallon of water). About half of the core pieces from the top of Plug 1 were also inundated in this 128°F brine at 28-d age. The remainder of the cores were kept in sealed plastic tubes at laboratory ambient temperature 68°-78°F. The samples from Plug 3 were inundated in a tank of saturated brine at ambient temperature in the laboratory. The samples from Plug 4 were inundated in a tank of fresh water at laboratory ambient temperature.

3.3 Nondestructive Test Data

Bulk Density -- The bulk density data for all samples and cores are listed in Table A-1, A-2, A-3, and A-4 in Appendix A and are summarized in Table 3-2. The densities of specimens at 28 d are greater than the fluid weight for all grout mixtures except for the recirculated specimens which are about the same. The increase in density was 3% to 5% for the first three mixtures that contained brine mixing water (and stored in brine water) and 6% for the material made using fresh water for Plug 4 and stored in fresh water. A review of the data for individual specimens shows that the change in density from the initial reading to 1 yr is less than 1% for the three mixtures containing brine mixing water. No clearly consistent trend with increasing age within this small variation was found. The fresh water mixture for Plug 4 shows a consistent trend of increasing density with age--a 2% increase from 28 to 230 d and little change at 1 yr.

All the density data show a uniformly mixed grout in the field for each grout mixture. The small variation in density with time show the hardened grout as a dense and durable material.

Compressional Wave Velocity -- The compressional wave velocity for all specimens from all plugs show a steady increase with age in Table 3-3. This is to be expected for samples of competent grouts, particularly for those containing a significant portion of flyash (30% by volume). The cores from Plug 1 started with higher values at 16 and 28 d and then remained at approximately the same values as the surface-cast samples. These core samples had cured under the pressure of the fluid-filled hole above the plug (about 2000 psi) and the temperature of 128°F for the first 48 h until coring. The two mixtures with 30% and 36% salt-brine mixing water (Plugs 1, 2, and 3) had about the same compressional wave velocity through 1 yr of age. The samples of return grout from Plug 3 averaged about 5% less than the surface specimens at 28 d and compared to about a 3% reduction in density.

The fresh water mixture for Plug 4 had higher values of velocity throughout the 1-yr age--about 13% compared to the brine mixtures at 1 yr. This was caused by the higher cement content, lower water-cement ratio (and consequently higher density), and lack of salt in the mixing water. All of the data for compressional wave velocity show strong competent grouts and no deterioration with aging. The continuing hydration of the flyash and cement follows the intended trend of increasing soundness with time.

Dynamic Modulus -- The data for averages of dynamic modulus values are listed in Table 3-4. There is a wide variation in the data in Appendix A for the specimens from each plug as well as some variation in the readings on a specimen at different ages. The ideal specimen for the dynamic modulus excitation has a 6:1 length-to-diameter ratio Many specimens had ratios much less. The averages for Plug 1 have an increasing trend with time which agrees with the trend for compressional wave velocity and strength gain. The data for Plugs 2 and 3 are more variable with the values at 230 d being significantly higher than 28 d and an apparent reduction at 365 d. The data for the higher strength Plug 4 mixture shows an average variation of less than 10% from 28-d to 365-d age. The significance of the variations for the lower strength mixture for Plugs 2 and 3 will be studied at yearly intervals and reported in the future.

3.4 Destructive and Other Tests

Unconfined Compressive Strength -- A limited number of specimens were tested for unconfined compressive strength; the averages are listed in Table 3-5. For Plug 1, the surface cast samples had strengths of 2050 and 1540 psi at 27 d (average 1795 psi). The two pieces of core tested at 28 d had consistent strengths of 1710 and 1760 psi. The low strength of 700 psi for the piece of core tested at 16 d was probably caused by damage to the specimen as a result of the coring operation (a 50-ft core barrel operating at the end of a 3650-ft drill string). During coring of each of the three 50-ft lengths of core, the barrel jammed in the hole. The strengths of the six pieces of core at 230 d varied from 1590 to 3420 psi as further evidence of damage to specimens during the coring operation.

The strengths of the surface-cast samples for Plugs 2 and 3 were all above 2160 psi at 28-d age and showed little variation. The samples of recirculated grout from Plug 3 were slightly lower at an overall average of 2055 psi. The top 6 in. of the 6- x 12-in. cylinders showed strengths averaging 1840, while the average halfs were 2270. Of course, the length-to-diameter ratio was 1 instead of the usual 2 for standard cylinders for unconfined compressive strength. The higher strengths show the normal slight settling of the cement particles in grout before initial set.

The results of tests on these two grout mixtures (for Plugs 1, 2, and 3) with salt-brine mixing water generally agree with the laboratory data in Table 3-1. The strengths in situ in the plugs should be in excess of 2500 psi. The fresh water mixture for Plug 4 had a strength in excess of 6000 psi at 28 d; this resulted from the higher cement content, lower water-cement ratio, and lack of salt.

Porosity Measurements -- Samples of the cast specimens, cores, and recirculated returns were selected for an additional series of tests to determine porosity at approximately 80 d of age. The data are listed in Table 3-6. Both the water pycnometer and the T-4 methods with the material crushed to pass the 600-μm (30 mesh) sieve were used as a direct comparison between the two methods. The additional properties of as-received and dry density are also listed. For the Plug 1 mixture, the T-4 method showed an average increase of 9.5% in porosity compared to the water pycnometer method. For the Plug 2 and 3 mixture, the increase was 9% to 10%. The recirculated returns from Plug 3 showed a 7% increase. For the fresh-water mixture of Plug 4, the increase was less than 1%.

This data can be compared to the data for the lab studies in Table 2-7 which were all done by the water pycnometer method. The comparison indicates that effective porosities are greater for mixtures with brine-mixing water than for fresh-water mixtures.

Water Permeability -- Some of the cores from Plug 1 and surface-cast samples were subjected to water permeability tests (CRD-C48-73)[4] at both early ages of less than a month and greater than 1 yr. The specimens had been inundated in saturated brine as previously described. The results are listed in Table 3-7. For Plug 1, the surface-cast specimens and the core piece from Box 3 of core Barrel 2 had comparable permeabilities at the two early test periods. Different specimens were used at the 400-d age. Both showed reductions in permeability compared to the less than 1-mo data. The pieces of core from Box 8, Barrel 3, showed significantly higher permeabilities up to 1 mo; this could be a result of damage during the coring operation. The piece from Box 3 of Barrel 3 tested at 400 d is above the other core pieces but still less than the early age data from the same core barrel.

The data for the grout mixture from Plugs 2 and 3 exhibit reductions in permeability with time. The one specimen tested at 400-d age shows a significant reduction (to 0.2 µD). A comparison shows a consistent trend in lower permeabilities for the Plug 1 mixture with 30% salt compared to the mixture for Plugs 2 and 3 with 36% salt.

The fresh-water mixture for Plug 4 shows the lowest permeability at less than 1-mo age. The sample at 400-d age showed a higher permeability of 0.9 µD. Additional tests will be conducted to see if this is data scatter or a trend with time for samples inundated in fresh water.

Gas Permeability and Porosity -- ERDA 10 samples were sent to a commercial laboratory for determination of gas permeability and porosity at ages of 120 to 170 d. The data are listed in Table 3-8. The discussion of the data in Table 2-10 also applies to these data. The high temperature used to dry out the specimens may have altered the hydration product matrices. The permeabilities show a wide variation between core plugs drilled parallel (vertical) and perpendicular (horizontal) to the axis of the cylinder sample.

The porosity data for all of the surface sample determined by a differential pressure of 30 mm of mercury do not appear reasonable. The data for the core samples fall within the range of data in Table 3-6 for comparable samples.

At about 13 mo of age, four core samples were tested by the same commercial lab. Two of the samples were dried at 300°F for 4 h and had permeabilities of 117 and 323 µD. Two companion samples were tested without any drying and had permeabilities of 23 and 46 µD. This gives ratios of about 5 and 7 between the partially dried as-is specimens.

TABLE 3-1

Grout Mixture Data

	Units	Plug 1* 30% Salt	Plug 2 and 3** 36% Salt	Plug 4 Fresh Water
Cement, Class C (SR)	lb/ft^3	42.90	39.58	54.83
Litepoz 3 (flyash)	lb/ft^3	14.47	13.35	18.50
Salt Gel (attapulgite)	lb/ft^3	1.15	1.06	---
Bentonite Gel	lb/ft^3	---	---	1.47
Salt D44	lb/ft^3	10.77	14.15	---
Silica Sand D44	lb/ft^3	3.26	3.01	---
Dispersant D45	lb/ft^3	0.06	0.05	---
Dispersant D65	lb/ft^3	---	---	0.29
Calcium Chloride (51)	lb/ft^3	1.15	1.06	---
Water	lb/ft^3	36.6	39.3	36.0
Density	lb/ft^3	108.5	107.0	112.2
Density	lb/gal	14.5	14.3	15.0
Yield	ft^3/sack	1.5	1.7	1.2
Water Content	gal/sack	6.6	7.8	5.2
Water/Cement Ratio		0.85	0.99	0.66
Water/Cement and Flyash Ratio		0.64	0.74	0.49
Thickening Time	h:min	4:35	7:45	5:05
Unconfined Compressive Strength				
24 h	psi	712	420	1210
48 h		1543	1032	1522
72 h		1888	1275	2080

Notes:

*Plug 1 cured at 128°F, 2445 psi

**Plug 2 and 3 cured at 125°F, 2112 psi

***Plug 4 cured at 80°F, 445 psi

TABLE 3-2

Average Bulk Density (lb/ft^3)

	Fluid Density in Field	Age at Test (days) 16	28	72	230	365
Plug 1						
Surface Samples	110.7	114.6	114.6	115.3	115.2	114.1
No. of Tests	--	2	4	2	10	6
Cores	110.7	115.9	115.8	116.1	114.6	114.6
No. of Tests	--	3	5	3	16	12
Plug 2						
Surface Samples	109.7	--	114.9	--	114.5	114.2
No. of Tests			2		6	4
Plug 3						
Surface Samples	110.0	--	113.4	--	113.6	113.5
No. of Tests			2		3	5
Recirculated Samples	110.0	--	109.8	--	--	--
No. of Tests			4			
Plug 4						
Surface Samples	111.4	--	116.5	--	118.2	118.6
No. of Tests			2		11	10

TABLE 3-3

Average Compressional Wave Velocity (Vp, ft/s)

	Age at Test (days)					% Increase 28 to 365 d
	16	28	72	230	365	
Plug 1						
Surface Samples	8,271	8,934	10,180	10,156	10,463	+17
No. of Tests	2	4	2	12	6	
Cores	8,883	9,360	10,164	10,065	10,209	+ 9
No. of Tests	3	5	3	22	12	
Plug 2						
Surface Samples	--	8,692	--	10,227	10,547	+21
No. of Tests		2		7	4	
Plug 3						
Surface Samples	--	8,840	--	9,813	10,326	+17
No. of Tests		2		5	4	
Recirculated Returns	--	8,418	--	--	--	--
No. of Tests		4				
Plug 4						
Surface Samples	--	11,259	--	11,518	12,022	+ 7
No. of Tests		3		12	10	

TABLE 3-4

Average Dynamic Modulus E (10^6 psi)

	Age at Test (days)				
	16	28	72	230	365
Plug 1					
Surface Samples	0.94	1.13	1.60	1.85	1.84
No. of Tests	2	4	2	7	5
Cores	1.15	1.53	1.86	1.75	1.95
No. of Tests	3	3	5	6	6
Plug 2					
Surface Samples	--	1.23	--	1.81	1.54
No. of Tests		2		5	3
Plug 3					
Surface Samples	--	1.11	--	2.15	2.02
No. of Tests		2		4	4
Recirculated Returns	--	1.01	--	--	--
No. of Tests		4			
Plug 4					
Surface Samples	--	2.46	--	2.52	2.29
No. of Tests		2		11	10

TABLE 3-5

Average Static Unconfined Compressive Strength (psi)

	Age at Test (d)		
	16	27 to 29	230
Plug 1			
Surface Cast	1,770	1,795	--
No. of Tests	1	2	
Cores	700	1,735	2,579
No. of Tests	1	2	6
Plug 2			
Surface Cast	--	2,230	--
No. of Tests		2	
Plug 3			
Surface Cast	--	2,220	--
No. of Tests		2	
Recirculated Return	--	2,056	--
No. of Tests		8	
Plug 4			
Surface Cast	--	6,333	--
No. of Tests		2	

TABLE 3-6

Porosity, ERDA 10 Samples
(80-d age)

	Density as Received (g/cm^3)	Dry Density (g/cm^3)	Porosity, % Pycnometer Method	Porosity, % T-4, crushed to pass 60 µm (30 mesh) Sieve
Plug 1				
Surface cast	1.81	1.46	35.5	43.7
Core, Bbl 2 Box 1	1.88	1.52	31.4	41.7
Core, Bbl 2 Box 2	1.83	1.41	35.5	44.8
Core, Bbl 2 Box 3	1.83	1.41	35.6	45.0
Core, Bbl 3 Box 3	1.86	1.47	33.1	43.1
Core, Bbl 3 Box 8	1.85	1.44	34.9	44.0
Core, Bbl 3 Box 10	1.84	1.43	35.5	44.3
(Core Average)	(1.85)	(1.45)	(34.3)	(43.8)
Plug 2				
Surface cast	1.81	1.48	35.5	44.3
Plug 3				
Surface cast	1.79	1.46	34.4	45.0
Recirculated Returns				
Cylinder 1	1.71	1.35	39.3	48.1
Cylinder 2	1.77	1.41	39.3	47.0
Cylinder 3	1.76	1.39	39.0	46.2
Cylinder 4	1.75	1.37	42.8	46.9
(Recirculated Returns Average)	(1.75)	(1.38)	(40.1)	(47.0)
Plug 4				
Surface cast	1.82	1.46	40.4	41.3

TABLE 3-7

ERDA 10 Samples Water Permeability

Specimens	Age, (days)	Water Permeability $ft^3/s/ft^2 \times 10^{-12}$	Water Permeability Microdarcies (μD)
Plug 1			
Surface Cast	18-22	30.8	1.0
Surface Cast	25-29	15.4	0.8
Surface Cast	400	3.2	0.1
Plug 1			
Core Bbl 2 Box 3	18-22	35.0	1.1
Core Bbl 2 Box 3	25-29	26.5	0.8
Core Bbl 2 Box 3	400	13.3	0.4
Plug 1			
Core Bbl 3 Box 8	18-22	109.7	3.5
Core Bbl 3 Box 8	25-29	211.2	6.7
Core Bbl 3 Box 3	400	36.4	1.2
Plug 2			
Surface Cast	18-22	119.0	3.8
	25-29	83.2	2.6
	400	5.4	0.2
Plug 3			
Surface Cast	18-22	183.7	5.8
	25-29	138.6	4.4
Plug 4			
Surface Cast	18-22	8.3	0.2
	25-29	3.1	0.1
	400	28.5	0.9

TABLE 3-8

Gas Permeability and Porosity

Specimens	Permeability,[a] Microdarcies (μD) Vertical	Horizontal	Porosity, Percent (%)[b] Vertical	Horizontal
Plug 1				
Surface Sample	240	<20	2.3	1.9
Core Bbl 2 Sample 1			39.4	
Core Bbl 2 Sample 3			45.4	
Core Bbl 2 Sample 4	50	<20	31.7	32.7
Core Bbl 2 Sample 6			44.9	
Core Bbl 3 Sample 3			44.6	
Core Bbl 3 Sample 8			39.3	
Core Bbl 3 Sample 10			47.7	
Plug 2				
Surface Sample	<20	<20	6.7	4.0
Plug 3				
Surface Sample	<20	480	5.9	2.7
Recirculated Return	20	<20	12.6	2.5
	<20	<20	4.0	8.5
Plug 4				
Surface Sample	370	420	24.4	26.6

NOTES:

General: Both the permeability test and the porosity tests were made on the same plug for the same sample.

a. Permeability test was made using the soap-bubble method, that measures the flow of air through the sample by movement of a soap bubble in a pipette on the downstream side using an upstream pressure of 300 mm of mercury.

b. Bulk volume was measured in cubic centimeters on each dried sample; then, using the Washburn-Bunting method, a 30-in. vacuum was pulled on the sample. To extract the air filling the pore space, this air volume was then moved to the top of the porosimeter where it was measured direct in cubic centimeters. The pore space divided by bulk volume = porosity.

4. PETROGRAPHIC AND CHEMICAL INVESTIGATIONS

Materials characterization based on studies using X-ray diffraction, light microscopy, and scanning electron microscopy (SEM) were made. Three memoranda giving the results are included in Appendix B. The data may be summarized as follows:

The ERDA 10 work consisted of examination of grout core from Plugs 1, 2, and 3 - samples at one or two ages along with control specimens and some of the materials used in the grout. No salt gel or drilling mug was detected in any of the grout cores taken from Plug 1 downhole. This indicated that they were satisfactorily displaced by the grouting operation. No effects due to the temperature of 128°F or pressure were recognizable. Substantial amounts of material characterized by an X-ray diffraction peak at 7.84 Å (0.78 nm) were present in the grout samples. It was believed to be the beta form of calcium monochloraluminate hydrate ($3\ CaO \cdot Al_2O_3 \cdot CaCl \cdot 10H_2O$). This material is commonly called Friedel's salt. Its presence was believed to be the normal consequence of use of the brine-mixing water and is not thought to be harmful. However, future work will include studies of specimens at later ages to verify this belief. The SEM photomicrographs were useful in the study of the microstructure of the grout samples, and are included with the memo in Appendix B.

Examination of cores from a block of salt embedded in grouts made with and without salt-saturated mixing water showed that the use of fresh water resulted in open contact surfaces (and no bonding) because some of the salt was dissolved by contact with the water in the grout mixture.

Examination of five cements by X-ray diffraction indicated that none of them contained detectable crystalline tricalcium aluminate (C_3A). The composition and relative amounts of compounds of three expansive cements are also included in the memo in Appendix B.

Several samples of the core and a surface sample were delivered to the Dowell Laboratory in Tulsa. The memorandum from L. B. Spangle including the SEM photomicrographs is Appendix C. The surface sample and the drilled core sample were found to be very similar in the tests. The surface sample when analyzed by the SEM had the cubic salt structure throughout its porosity. The drilled sample had a more glazed appearance. There were other slight variations in permeability and degree of hydration.

Study of a sample of 17-yr-old grout that had filled a hole in the rock salt of Duval Mine[6] showed that its microstructure was similar to the ERDA 10 samples. At this age the contact surface between the grout and the rock wall was tight; there was no evidence of deterioration.

Samples of the cements and flyash used in the Borehole Plugging Program were analyzed. The chemical compositions and physical property data for the ChemComp, ChemStress, and Type III used in the original five laboratory study mixtures are listed in Table 4-1. The data for the Class C and H cements and flyash are listed in Tables 4-2 and 4-3.

TABLE 4-1

Chemical Analysis and Physical Properties of Cements (Part 1)

	ChemComp	ChemStress	Type III
WES Sample No.	RC762	RC749	RC777
Date Sampled	3/8/76	12/74	2/7/77
Fineness, g/cm^2	3980	3512	4560
C_3A, %	-	-	-
C_2S, %	-	-	-
C_3S, %	-	-	-
C_4AF, %	-	-	-
SiO_2, %	20.1	15.5	23.7
Al_2O_3, %	4.4	9.2	3.5
Fe_2O_3, %	2.7	2.1	3.2
MgO, %	0.8	1.4	1.6
SO_3, %	5.8	15.3	3.3
Loss on Ignition, %	1.5	1.6	0.7
CaO, %	63.9	55.0	63.4
Air Content, %	9.0	-	7.2
7-d Comp. Strength, psi	4390	-	4470
Initial Set, h:min	1:45	0:35	2:40
Final Set, h:min	5:00	1:25	5:05
Sp Gr	3.12	3.06	-
Alkalies, Total as Na_2O, %	0.25	0.34	0.46
Na_2O, %	0.11	0.13	0.30
K_2O, %	0.22	0.32	0.25

TABLE 4-2

Chemical Analysis and Physical Properties of Cements (Part 2)

	Class C (SR)					Class H						
	El Toro 35 Odessa SWPC	El Toro 35 Odessa SWPC	Incor	Incor	Incor	Odessa SWPC	Incor	San Antonio Longhorn Kaiser	Amarillo SWPC			Incor
WES Sample No.	RC800A	RC806	RC8018	RC804	RC835	RC785	RC805	RC821	RC825	RC825	RC837	RC836
Date Sampled	2/8/78	4/20/74	2/8/78	4/19/78	2/12/79	4/19/78	4/19/78	11/8/78	11/8/78	1/30/79	2/1/79	2/12/79
Fineness cm^2/g	4140	4060	4750	4580	4030	2840	2260	2270	3380	3440	3100	2570
C_3A, %	2.8	0.8	2.3	1.8	5.6	3.2	0	4.6	5.8	5.3	3.7	4.8
C_2S, %	6	7	18	16	38	27.7	23	27	23	20	23	34
C_3S, %	72	70	58	61	37	52.1	57	49	56	58	57	41
C_4AF, %	14	15	13	13	12	9.1	15	13	9	9	10	12
SiO_2, %	20.9	20.9	21.5	21.5	23.0	22.4	23.0	22.2	22.5	22.2	[illegible]	23.1
Al_2O_3, %	4.0	3.5	3.6	3.5	4.6	3.7	3.0	4.5	4.1	3.9	3.5	4.3
Fe_2O_3, %	4.6	5.0	4.3	4.4	3.9	4.0	5.2	4.3	3.0	3.0	3.3	3.9
MgO, %	1.0	1.0	2.4	2.5	2.0	1.8	2.3	0.7	1.9	2.0	1.6	2.3
SO_3, %	2.6	2.4	3.0	2.7	2.7	2.1	1.3	1.7	2.4	2.3	2.2	2.2
Loss on Ignition, %	0.5	0.59	1.8	0.97	0.4	0.51	0.37	2.6	0.6	0.7	0.6	0.5
CaO, %	66.3	65.4	63.5	64.2	62.9	65.0	64.8	63.6	65.2	64.9	65.3	63.6
Air Content, %	8.3	8.5	8.4	9.0	9.2	9.0	10.8	10.0	8.0	8.8	10.2	9.8
7-d Comp. Strength, psi	5220	4250	4720	4130	4260	1970	1510	1260	3950	3830	3710	2200
Initial Set, h:min	2:50	3:05	3:05	3:30	2:55	4:30	3:45	3:50	4:05	4:05	3:30	3:30
Final Set, h:min	5:20	5:00	6:25	6:15	4:15	7:10	6:10	5:25	5:35	6:15	5:40	6:00
Sp Gr	-	-	-	-	-	-	-	3.11	3.18	3.19	-	-
Alkalies, Total as Na_2O, %	0.35	0.32	0.32	0.43	0.42	0.43	0.50	0.36	0.39	0.39	0.30	0.31
Na_2O, %	0.23	0.21	0.08	0.11	0.11	0.30	0.14	0.06	0.23	0.23	0.19	0.14
K_2O, %	0.18	0.17	0.36	0.48	0.48	0.20	0.55	0.46	0.25	0.25	0.17	0.56

C_3A = (2.65X% Al_2O_3) - (1.69 X% Fe_2O_3)

NOTE:

SWPC - Southwestern Portland Cement Co., Odessa or Amarillo Plants

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

TABLE 4-3

Chemical Analysis of Flyash

Source	Dowell Plant Artesia, NM Harrinton Power Plant	Dowell Plant Artesia, NM Trinity Portland, Texas Electric, Big Brown Plant, Fairfield
Date Tested	12 February 1979	17 November 1977
SiO_2, %	39.9	49.5
Al_2O_3, %	21.1	20.7
Fe_2O_3, %	5.34	5.5
CaO, %	26.2	17.9
MgO, %	3.6	3.3
SO_3, %	1.5	1.0
Total Alkalies, as Na_2O, %	1.73	1.17
Na_2O, %	1.14	0.64
K_2O, %	0.89	0.80
Loss on Ignition, %	0.2	0.4
Fineness, g/cm^2	3740	2920
Specific Gravity	2.63	-
Autoclave Expansion, %	0.08	-
Lime-Pozzolan Strength, psi	1670	1330

5. CONCLUSIONS AND RECOMMENDATIONS

The data for the five laboratory mixtures through 2 yr of aging (both in and out of simulated groundwater at the WIPP site) confirm the visual observations that there is no evidence of deterioration of any of the samples. The variations of compressional wave velocity and dynamic modulus are random and within the range of accuracy of the measurement techniques for the size of specimen. The push-out bond strengths (against black iron pipe) were higher for the two mixtures with brine mixing water. The unrestrained length change data show that all mixtures have small length changes through 2-yr aging. Moisture loss from the bars stored in plastic bags is causing the length reductions. All of the inundated bars are increasing in length expect Mixture 4 with additional pozzolan filler which is maintaining its initial length. The data on change in mass for the inundated bars have a steadily decreasing rate of mass increase (less than 0.5% mass increase for the second year). The changes in porosity and bulk solid density do not have a clearly defined trend. Future data may help to understand significance.

Water permeability at 2-yr age is less than at 30 d for all mixtures tested. All values are less than 0.9 μD. Gas permeability and porosity testing were performed by a commercial laboratory using standard methods for rock cores. The high-temperature process may have altered the hydration product matrix and resulted in the relative high gas-permeability data. Also the low differential pressure used to determine porosity gave some very low values for the two mixtures with brine. The formation of the alpha and beta forms of chloroaluminate in the two mixtures with brine mixing water may be the cause of the lower values of gas permeability.

Testing of field samples from the ERDA 10 field-plugging operation show the three grout mixtures as stable and durable materials. The core samples obtained from the top of Plug 1 about 48 h after placing compare closely with cylinder samples cast at the surface. This lends confidence to the data from specimens cast at the surface during an operation being representative of the in-place plug material. The bulk-density data show uniformity of each in the field; there is little variation with time through 1-yr aging. All of the data for compressional wave velocity show strong competent grouts and no deterioration with aging. The continuing hydration of cement and flyash is following the intended trend of increasing soundness with time. The average dynamic modulus data for Plug 1 show an increasing trend with time and agree with the expected trend for compressional wave velocity and strength gain. The values of dynamic modulus for the mixtures for the other three plugs are highest at 230 d with an apparent average reduction of 5% to 15% of 1 yr. These will continue to be monitored at yearly intervals to determine the significance of this rather imprecise nondestructive test method for specimens with low L/D ratios.

The unconfined compressive strengths for the two mixtures (for Plugs 1, 2, and 3) with brine mixing water generally agree with the preparatory laboratory data (in Table 3-1). The strengths in situ in the plugs should be in excess of 250 psi. The fresh-water mixture for Plug 4 had a strength in excess of 6,000 psi at 28 d, resulting from the higher cement content, lower water/cement ratio, and no salt.

Water permeability data for the five laboratory mixtures show very low values - about 1.4 μD at 1 mo and significantly less at later ages. The water-permeability data for the ERDA 10 plug mixtures also show significant reductions at later ages from initial values of 7 μD and less. These data confirm the soundness and durability of the grouts through 1 and 2 yr of aging.

Gas-permeability data from testing performed by a commercial laboratory are included in the report. The specimen preparation included drying at 200°F and 300°F which may have altered the matrix of hydration productions.

Porosity data determined by different methods and at various ages are reported. The significance of these data are not evident at this time. The planned future program of geochemical studies will help to reveal the microstructure of the hardened cement and may reveal the significance of the porosity data for grouts with and without brine mixing water.

Since one parameter of major concern is the effect of time on borehole plugging, the limited data for the 17-yr-old grout from the Duval Mine[6] are considered significant. The cement and brine mixing water were similar to the ERDA 10 materials. The exposure for 17 yr is much longer than any of the current laboratory studies in this program. The constancy of composition as compared with the ERDA 10 grout samples is encouraging. In addition, the tight contact of the grout to the rock-salt wall is also promising.

For grouts used in the downhole environment of Southeastern New Mexico, salt in the mixing water is desirable. The examination of the two laboratory mixtures and the ERDA 10 mixtures with brine mixing water (when placed in a halite block) have shown that a tight contact of the hardened grout to the halite is achieved.

All of the existing specimens used for nondestructive testing will continue to be monitored. The data generated to date will provide the basis for the proposed geochemical studies program to be sponsored by ONWI. Samples of grouts with ages up to 3 yr and cured under differing conditions will be available at the start of the proposed very comprehensive and detailed study program.

Samples of cementing materials reasonably available at the WIPP site will continue to be evaluated. Proportioning studies will also continue as a part of the evaluation program. Samples molded in the field during plugging operations will be added to the long-term durability studies to increase the data base for future decisions related to the planning of the borehole plugging program.

References

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[2]C. W. Gulick, Jr., Borehole Plugging - Materials Development Program, SAND78-0715, (Albuquerque: Sandia Laboratories, June 1978).

[3]C. W. Gulick, Jr., Borehole Plugging Program - Plugging of ERDA No. 10 Drill Hole, SAND79-0789 (Albuquerque: Sandia Laboratories, 1978).

[4]Corps of Engineers, U.S. Army, Handbook for Concrete and Cement [Vicksburg, Mississippi: Waterways Experiment Station, August 1949 (with Supplements through September 1978)].

[5]API Recommended Practice 10B, Testing Oil-Well Cements and Cement Additives (Dallas, Texas American Petroleum Institute, Production Department, 300 Corrigan Tower Bldg., April 1977).

[6]A. D. Buck and J. P. Burkes, "Examination of Grout and Rock From Duval Mine, New Mexico," U.S. Army Engineer Waterways Experiment Station, CE, Miscellaneous Paper No. SL-79-16, Vicksburg, Mississippi, 1979.

APPENDIX A

Test Data for ERDA 10 Samples

TABLE A-1

Plug 1 Nondestructive Test Data

Specimen No. (Age, Days →)	Size	Condition	Density lb/ft^3 16	27	72	230	365	Compressional Wave Velocity, v_p ft/s 16	27	72	230	365	Dynamic Modulus, E, 10^6 psi 16	27	72	230	365
Batch 1																	
#1	6 x 10.9	Brine at 128°F		115.3		115.6			8588		10042			1.0		2.1	
	Core	Brine at 128°F				116.2					10236					1.7	
	Shell	Brine at 128°F									10394						
#2	6 x 11.3	Brine at 128°F	115.3	114.6	115.3	115.9	115.9	8330	9232	10247	10236	10581	0.9	1.1	1.6	1.7	1.7
#3	6 x 5.2	Brine at 128°F				113.4	112.8				9420	10233					
#1	3 x 5.1	Brine at 128°F				115.9	115.3				10119	10897				1.6	1.5
#2	3 x 5.4	Brine at 128°F				114.0	113.4				9874	10323				1.8	1.7
Batch 2																	
#1	5 x 11.6	Brine at 128°F	114.0	114.6	115.3	115.3	114.0	8211	9319	10112	10284	10623	1.0	1.3	1.6	1.8	1.8
#2	6 x 10.8	Brine at 128°F				115.5			8626		10227			1.1		1.8	
	Core	Brine at 128°F				115.6					10493						
	Shell	Brine at 128°F									10344						
#1	3 x 6.0	Brine at 128°F				114.6	113.4				10118	10118				2.4	2.4
Core Bbl 1																	
Box 1	4 x 8.0	Brine at 128°F	115.9	115.9	115.9	115.3[a]		8946	9585	10152	9661[a]		1.1	1.6	2.1	1.8[a]	
	Core	Brine at 128°F					116.5				10697	10455				1.9	1.8
	Shell	Brine at 128°F					114.6				10074	10547					
Core Bbl 2																	
Box 4	4 x 8.0	Brine at 128°F	114.6	114.6	115.3	115.3[a]		8813	9608	10060	9743						
	Core	Brine at 128°F					115.9		9743	10154							
	Shell	Brine at 128°F							9681								
Core Bbl 3																	
Box 8	4 x 7.8	Brine at 128°F	117.1	117.1	117.1	117.1[a]		8891	9478	10281	10186						
	Core	Brine at 128°F					115.9				10877	10333					
	Shell	Brine at 128°F					117.8				9558	10625					
Core Bbl 1																	
Box 2	4 x 4.2	Brine at 128°F				105.3[b]	106.5[b]				8432[b]	8639[b]					
Core Bbl 2																	
Box 1	4 x 6.8	Plastic Bag				116.6[c]					10193[c]						
2	4 x 7.4	Plastic Bag				114.5[c]					10704[c]	10417					
2	4 x 9.0	Brine at 128°F				114.0	114.0				10273	10417					
3	4 x 8.2	Plastic Bag				114.6[c]					9761[b]						
4	4 x 9.6	Brine at 128°F				113.4	113.4				10162	10288					2.3
6	4 x 10.0	Brine at 128°F				114.0	114.0				10011	10297					2.1
3	4 x 8.6	Brine at 128°F				115.9	115.3				10335	10611					1.9
7	4 x 6.8	Brine at 128°F				115.9	115.9				10416	9534					
7	4 x 5.9	Plastic Bag				115.8[c]					10034						
8	4 x 8	Plastic Bag		115.9[c]					9178[c]					1.4			
9	4 x 6.4	Plastic Bag				115.2[c]					10336[c]						
10	4 x 5.5	Plastic Bag				116.6[c]					10336[c]						
10	4 x 8	Plastic Bag		115.3[c]					8952[c]					1.4			
11	4 x 5.8	Brine at 128°F				114.6	115.3				10156	10372					

Notes:

a. The specimens indicated were cored at the indicated ages to give a better L/D ratio for improved Dynamic E readings; Core was 2.95 x 7.8 in.

b. These specimens were destructively tested for unconfined compressive strength; therefore no further testing.

c. This core specimen was close to the top of the plug and had partial contamination with drilling mud. These values were omitted from average values.

TABLE A-2

Plug 2 Nondestructive Test Data

Specimen No. (Age, Days)	Size	Density (lb/ft^3) 230	Density (lb/ft^3) 365	Compressional Wave Velocity, v_p (ft/s) 230	Compressional Wave Velocity, v_p (ft/s) 365	Dynamic Modulus, E, 10^6 psi 230	Dynamic Modulus, E, 10^6 psi 365
Surface #1	6 x 11.6	114.6	-	10176	-	1.8	-
#1	Core[a]	114.6	-	10483	10168	1.9	1.8
#1	Shell	114.6	114.0	10130	10000	-	-
#2	6 x 11.5	114.6	114.6	10195	10531	1.8	1.5
#3	6 x 11.4	114.6	114.6	10260	10486	1.7	1.6
#4	6 x 11.4	115.2	114.6	10372	10602	1.8	1.5
#5	6 x 5.5	113.4	112.8	9963	b	-	-

NOTES:

General - All specimens cured in saturated salt (NaCl) brine at 128°F starting at 28-d age.

a. The specimen was cored at 230 d to give a better L/D ratio for improved Dynamic E readings, core 2.95 x 7.80 in.

b. Specimen used for permeability testing.

TABLE A-3

Plug 3 Nondestructive Test Data

Age, Days / Specimen No.	Size	Density lb/ft^3 28	230	365	Compressional Wave Velocity, v_p ft/s 28	230	365	Dynamic Modulus, E, 10^6 psi 28	230	365
Surface #1	6 x 11.8		113.3	113.3		9375			1.7	
#1	Core[a]		114.3	113.4		10588	10465		1.7	1.6
#2	6 x 11.7		113.8	114.0		10157	10598		1.7	1.6
#3	6 x 5.7		110.9	111.5		9896	10465		-	1.6
#1	3 x 6.0		114.6	113.4		9804	10204		2.6	2.5
#2	3 x 5.9		114.6	114.6		9834	10035		2.6	2.4
#2	6 x 12	113.4	b		8757					
#2	6 x 12	113.4	b		8922					
Recirculated Return 1	6 x 12	108.4			8295				1.0	
2	6 x 12	110.3			8487				1.0	
3	6 x 12	110.3			8600				1.0	
4	6 x 12	110.3			8288				1.0	
5	6 x 12	101.5	c		6083	c			0.35	c

NOTES:

General - All specimens cured in saturated salt (NaCl) brine at lab ambient temperature 68° to 78°F.

a. The specimen was cored at 230 d to give a better L/D ratio for improved Dynamic E readings, core 2.95 x 10.75 in.

b. Specimen broken at 28-d age for unconfined compressive strength.

c. Recirculated return sample No. 5 contaminated with drilling, omitted from average values.

TABLE A-4

Plug 4 Nondestructive Test Data

Age, Days / Specimen No.	Size	Density lb/ft^3 28	Density lb/ft^3 230	Density lb/ft^3 365	Compressional Wave Velocity, v_p ft/s 28	Compressional Wave Velocity, v_p ft/s 230	Compressional Wave Velocity, v_p ft/s 365	Dynamic Modulus, E, 10^6 psi 28	Dynamic Modulus, E, 10^6 psi 230	Dynamic Modulus, E, 10^6 psi 365
Surface #1	6 x 11.8		117.1	117.1		11563			2.8	-
#2	6 x 11.7		117.1	117.8		11771			2.8	1.5
#3	6 x 12		117.1	-		11647	-		2.8	1.5
#3	Core[a]		117.1	-		11923	10645		3.1	3.0
#3	Shell		-	118.4		11686	11883		-	-
#1	3 x 5.6		119.0	119.0		11483	11210		2.2	2.2
#2	3 x 5.6		117.8	118.4		10853	12282		2.3	2.2
#3	3 x 5.6		119.6	119.6		11563	11563		2.2	2.0
#4	3 x 5.4		118.4	119.0		11646	11355		2.0	1.9
#5	3 x 5.6		119.6	119.6		11280	12847		2.6	2.1
#6	3 x 5.9		119.6	119.6		11435	12608		2.6	2.6
#7	3 x 6.0		117.8	117.8		11364	12500		2.7	2.5
	6 x 12	116.5	b		11274	b		2.4	b	
	6 x 12	116.5	b		11244	b		2.5	b	

NOTES:

General - All specimens cured in fresh water at lab ambient temperature 68° to 78°F.

a. The specimen was cored at 230 d to give a better L/D ratio for improved Dynamic E reading. Core 2.95 x 11.8.

b. Specimens broken at 28-d for unconfined compressive strength.

TABLE A-5

Unconfined Compressive Strength

Plug No.	Specimen No.	Size (in.)	Curing Condition	Age at Test (days)	Unconfined Compression Strength (psi)
1	Surface, Batch 2	6 x 6	Cylinder Mold	19	1770
	CB 3, Box 10	4 x 8	Plastic Bag	19	700
	Surface, Batch 1	6 x 10.9	Cylinder Mold	27	1540
	Surface, Batch 2	6 x 10.8	Cylinder Mold	27	2050
	CB 3, Box 8	4 x 8	Plastic Bag	29	1710
	CB 3, Box 10	4 x 8	Plastic Bag	29	1760
	CB 2, Box 1	4 x 6.8	Brine @ 128°F	230	3420
	CB 2, Box 2	4 x 7.4	Brine @ 128°F	230	2230
	CB 2, Box 3	4 x 8.2	Brine @ 128°F	230	3340
	CB 3, Box 7	4 x 5.9	Brine @ 128°F	230	3065
	CB 3, Box 9	4 x 6.4	Brine @ 128°F	230	1590
	CB 3, Box 10	4 x 5.5	Brine @ 128°F	230	1830
2	Surface, Cast	6 x 12	Cylinder Mold	28	2160
	Surface, Cast	6 x 12	Cylinder Mold	28	2300
3	Surface, Cast	6 x 12	Cylinder Mold	28	2230
	Surface, Cast	6 x 12	Cylinder Mold	28	2210
	Recirculation #1	1.9 x 3.9 Top	Cylinder Mold	29	1570
	Recirculation #1	1.9 x 3.9 Bottom	Cylinder Mold	29	2080
	Recirculation #2	1.9 x 3.9 Top	Cylinder Mold	29	2060
	Recirculation #2	1.9 x 3.9 Bottom	Cylinder Mold	29	2460
	Recirculation #3	1.9 x 3.9 Top	Cylinder Mold	29	1950
	Recirculation #3	1.9 x 3.9 Bottom	Cylinder Mold	29	2255
	Recirculation #4	1.9 x 3.9 Top	Cylinder Mold	29	1790
	Recirculation #4	1.9 x 3.9 Bottom	Cylinder Mold	29	2280
	Recirculation #5	1.9 x 3.9 Top	Cylinder Mold	29	125
	Recirculation #5	1.9 x 3.9 Bottom	Cylinder Mold	29	630
4	Surface	6 x 12	Cylinder Mold	28	6190
	Surface	6 x 12	Cylinder Mold	28	6475

APPENDIX B

Memoranda of Petrographic Examinations

Corps of Engineers, USAE Waterways Experiment Station	Petrographic Report	Concrete Laboratory P. O. Box 631 Vicksburg, Mississippi
Project Examination of Grout Samples for Project ERDA 10		Date 4 January 1978 ADB

Background

1. The borehole known as ERDA 10, located in Eddy County, New Mexico, was filled with portland-cement base grout in October 1977. Forty-eight hours later a portion of Plug 1 was removed as 4-in. diameter core. Samples of this core, of control cylinders cast when the hole was filled, and of recirculated return grout from Plug 3 were received in the Concrete Laboratory (CL) on 17 October 1977. The 16-day-old specimens were examined at this time and at 28- to 31-day ages to answer the following two questions:

a. The hole was full of drilling mud before grout was introduced. Did the grout uniformly displace this mud upward or was there detectable contamination of the grout by the drilling mud?

b. It was anticipated that temperatures and pressures at or near the bottom of the 4431-ft deep hole would be about 128°F (53°C) and 2000 psi (14 MPa). Did either or both of these conditions have any detectable effect on the hydration products in the grout?

Samples

2. Samples of the materials used in the grout were received shortly after 17 October 1977. All of the samples that were examined are identified below:

	Received at 16 days age. Examined at Age, Days
Plug 1 samples	
Batch 1 control cylinder	16; 28
Batch 2 control cylinder	16; 28
Cores from 3556- to 3595-, from 3595- to 3623-, and from 3623- to 3673-ft depths	16
Core from 3623- to 3673-ft depths from	
Barrel 3 Box 8	28
Barrel 3 Box 10	28
Plug 2 samples	
Control cylinder	28
Plug 3 samples	
Control cylinder	28
Recirculated return cylinder 1	29
Recirculated return cylinder 3	29
Recirculated return cylinder 5	29
Recirculated return cylinder 6	31

WES FORM No. 1115
Rev Feb 1970

Material	Description
Incor "C" cement	Lone Star Portland Cement Co., Maryneal, Texas
Litepoz 3	Fly ash from Big Brown Plant of Texas Electric Co.
Salt Gel	Mixture of polygorskite,* clay, sodium chloride, and water

3. Although there were no core samples from Plugs 2 or 3 the cylinders of recirculated return material did represent grout from Plug 3. Cylinder 6 of that material consisted of about 3 in. of solid material in the bottom of the cylinder and 9 in. of salty water.

Test procedure

4. The hydrated grout samples were examined by X-ray diffraction (XRD) and by scanning electron microscope (SEM). The air contents of several of these samples were determined by CRD-C 42.[1] The cement, fly ash, and dry polygorskite clay like that used in the salt gel were examined by X-ray diffraction.

5. All of the X-ray diffraction patterns were made with an X-ray diffractometer using nickel-filtered copper radiation.

6. The hydrated grout samples were ground but not sieved, and were mounted on the X-ray diffractometer as tightly-packed powders in a static nitrogen atmosphere saturated with hot barium hydroxide solution. The purpose of the nitrogen and the barium hydroxide is to prevent carbonation and dehydration of the samples.

7. All of the hydrated grout X-ray patterns contained material characterized by a spacing at 7.84 Å.** One of the control samples was exposed to dry ice in a moist atmosphere and then X-rayed to see if this treatment had any effect on the position of this peak. A small sample of the cement was mixed with water, allowed to hydrate for 15 days, and then examined by X-ray diffraction to determine whether the 7.84-Å peak would be absent in the absence of chloride.

8. The unhydrated cement was X-rayed as a tightly-packed powder in a static nitrogen atmosphere. The fly ash and polygorskite clay were X-rayed as tightly-packed powders in air. A portion of the cement was examined as a grain immersion mount with a polarizing microscope to determine if it were contaminated.

9. Five percent of the polygorskite clay by weight was blended with a ground sample of the Batch 2 control sample of grout from Plug 1 and this

---

* The term polygorskite is preferred to attapulgite for this clay.

** 0.784 nanometres.

mixture was X-rayed. The intent was to determine the approximate amount of salt gel or drilling mud that would have to be in the grout to be detected by X-ray diffraction.

10. The sawed and ground surfaces of several specimens of grout were examined with a stereomicroscope to see whether drilling mud or other foreign material was present.

11. Small portions of the grout samples were freeze-dried. A fresh fracture surface was then made on the dried material. The new surface was coated with about 50 Å of carbon and about 150 Å of an 80 percent gold-20 percent palladium alloy. These coated surfaces were then examined by SEM and photographs were made of selected areas at different magnifications.

Results

12. The X-ray data for the grout samples may be summarized as follows:

a. There was no detected salt gel or drilling mud in any of the core samples or in the recirculated return samples. Since the 5 percent polygorskite clay that was added to one grout sample was detected by X-ray examination, if there were polygorskite contamination it was less than 5 percent.

b. All of the grout samples were similar. There were no detected and consistent differences between the surface control samples and the core or the recirculated return samples. This indicates that neither the combined nor the individual effects of elevated temperature and increased pressure on the hydration of the Plug 1 core and the Plug 3 recirculated return samples were significant.

c. There were no significant changes in the grout samples between the 16- and the 28- to 31-day ages.

d. The grout samples were characterized by the presence of small amounts of ettringite, large amounts of calcium hydroxide, substantial amounts of 7.84-Å material, and peaks in the diffraction pattern due to residual unhydrated portland cement. It is believed that the 7.84-Å material is the beta form of calcium monochloroaluminate hydrate ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$). Although this is not a normal hydration product of portland cement it is a reasonable reaction product when chloride is present; both NaCl and $CaCl_2$ were added to the grout mixtures. In many of the X-ray patterns there appeared to be an unresolved peak on the low angle shoulder of the 7.84-Å peak; it is likely that this represented the presence of the alpha form of the chloroaluminate. The identification of the 7.84-Å peak as a hydrated calcium chloroaluminate was supported when this peak was missing in the X-ray pattern of the hydrated cement with no added chloride. Calcium silicate hydrate was presumably present but cannot be readily detected in hydrated cementitious materials of the ages of these samples.

e. Halite (NaCl) ranged from not detected to abundant in the grout samples by X-ray diffraction. Its presence is indicated in the following tabulation:

	Halite
Plug 1	
Batch 1 control cylinder	Present
Batch 2 control cylinder	Not detected
Core - 3 pieces	Not detected
Plug 2	
Control cylinder	Abundant
Plug 3	
Control cylinder	Present
Recirculated return cylinder 1	Not detected
Recirculated return cylinder 3	Not detected
Recirculated return cylinder 5	Not detected
Recirculated return cylinder 6	Abundant

13. The halite was always detectable on sawed surfaces by taste. Its presence was also usually indicated on sawed surfaces by a white efflorescence that developed over a period of days. Other observations include:

a. Occasional small pieces of reddish rock (probably anhydrite) were found on sawed surfaces of the cores, but there was no significant amount of contamination by wall rock from the hole.

b. Examination of the core samples and of their sawed surfaces visually and with a stereomicroscope did not show any detected contamination by drilling mud.

c. The high insoluble residue (4.35 percent) found by chemical analysis of the cement indicated that it was contaminated. Examination of an immersion mount of cement with a polarizing microscope confirmed this conclusion and showed that the contaminant was fly ash.

14. Fly ash was not detected in the cement by X-ray diffraction and its detection would not be expected at the level shown chemically. X-ray examination did show that this was a high alite, low belite cement without any detectable tricalcium aluminate; the sulfate was present as anhydrite; a calcium aluminoferrite was present.

15. The crystalline phases in the "Litepoz 3" (fly ash) that were detected by X-ray were quartz, mullite, calcium oxide, and hematite. Those in the clay material used in the salt gel were mainly polygorskite clay with small amounts of 14-Å clay, clay-mica, and quartz.

16. Air void and other micrometric data are shown in Table 1 for seven samples of grout. The range of 1.6 to 3.3 percent air for the two control samples and the range of 2.0 to 2.6 percent air for the three core samples, all from Plug 1, indicate no significant changes due to pumping or to environment in the hole. The 5.6 percent air in the Plug 3 control cylinder indicates more air in this mixture; the additional pumping of the recirculated return cylinder 3 sample apparently caused its air content to increase to 8.0 percent.

17. The SEM photomicrographs did not show substantial differences between the control and plug samples at any age examined. This is in agreement with the other data. Photomicrographs 1a, 2a, and 4a show the typical appearance of the grout at 16- and 28-day ages. Photomicrographs 2b, 3b, 4b, and 5b are more highly magnified views that show the porous nature of the grout. Photomicrographs 6a and 6b are of a 28-day-old Type I portland cement paste with 30 percent fly ash that was made to normal consistency; the lower water content of this sample results in a much denser structure than seen in the grout samples. Photomicrograph 1b shows typical salt crystal development in a void in a control specimen of grout. Photomicrograph 3a shows an unusual appearance that was attributed to moisture pickup by the salt and its subsequent deposition during sample preparation. Photomicrograph 5a shows well developed platy crystals that may be the calcium monochloroaluminate hydrate that was identified by X-ray diffraction.

Discussion

18. The work that was done has shown that there was no appreciable contamination of the Plug 1 or Plug 3 grout by the drilling mud that it displaced as the hole was filled. The similarity of the grout from the ERDA 10 hole and of the control specimens indicated that neither the temperature nor the pressure in the hole had any appreciable effects on the hydration products that were formed. However, the presence of chloride did cause the formation of calcium monochloroaluminate hydrate in all of the samples. The presence of this compound probably caused the amount of ettringite formed to be lower than usual since some of its aluminum went into the chloride bearing compound. This is not considered significant since neither compound contributes to the strength of the grout. Halite was present in many samples.

REFERENCES

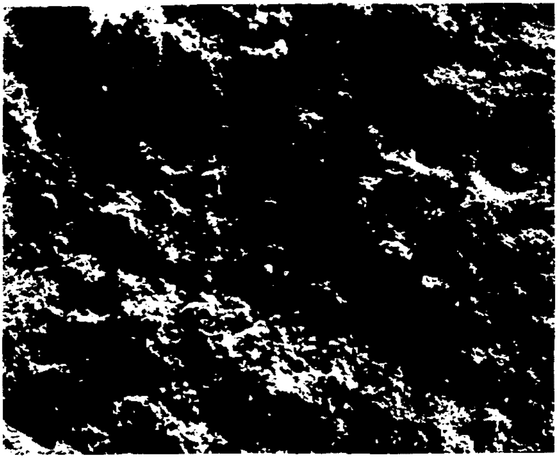
1. U. S. Army Engineer Waterways Experiment Station, CE, Handbook for Concrete and Cement, with quarterly supplements, Vicksburg, Miss., Aug 1949.

Table 1

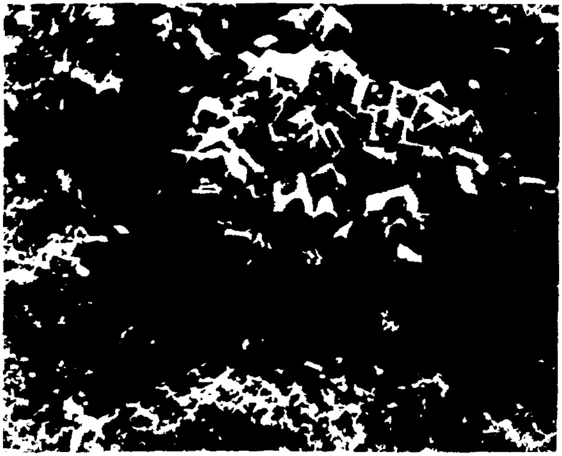
Micrometric Data* for Seven Grout Samples, Project ERDA 10

Micrometric Data, %	Plug 1 Samples: Control Cylinder 1	Plug 1 Samples: Control Cylinder 2	Plug 1 Samples: Core, in 3556- to 3595-ft Interval	Plug 1 Samples: Core, in 3595- to 3623-ft Interval	Plug 1 Samples: Core, in 3623- to 3673-ft Interval	Plug 3 Samples: Control Cylinder	Plug 3 Samples: Recirculated Return Cylinder 3
Entrapped air	3.3	1.6	2.4	2.6	2.0	5.6	8.0
Quartz	2.8	2.6	3.6	3.1	4.0	2.1	3.0
Paste	93.9	95.8	94.0	94.3	94.0	92.3	89.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

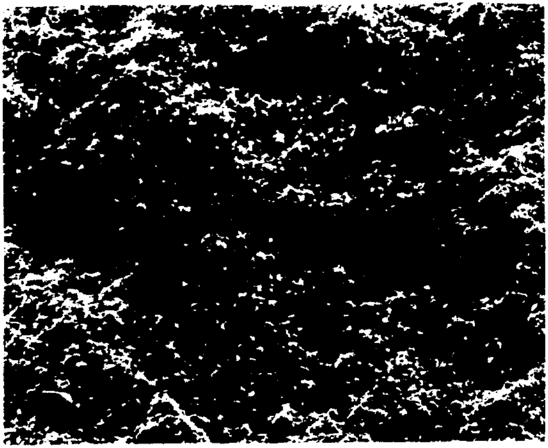
* CRD-C 42-71, Reference 1.



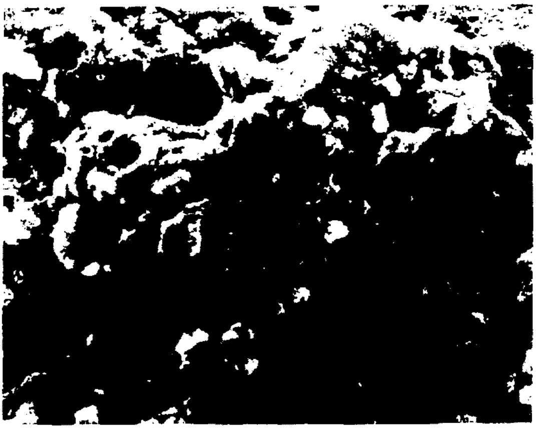
Photomicrograph 1a. Twenty-eight-day-old grout sample from Batch 1 control for Plug 1, X88. Typical of both batches and also of 16-day-old controls.



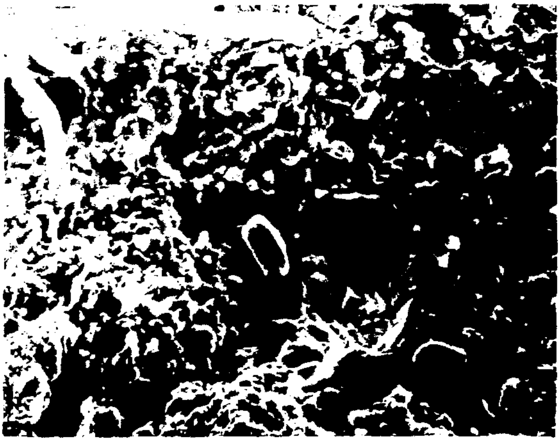
Photomicrograph 1b. Enlargement of halite crystals in void in center part of 1a, X440.



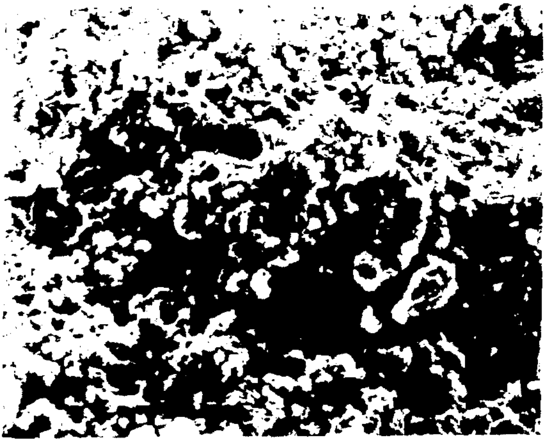
Photomicrograph 2a. Twenty-eight-day-old grout sample, core from Plug 1, Barrel 3, Box 8, X170. Similar in appearance to the control in 1a.



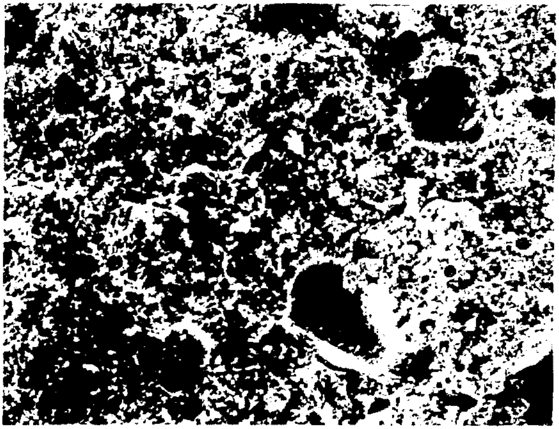
Photomicrograph 2b. Same as above, X1700. Note the porous appearance. This appears to be calcium silicate hydrate coating residual cement grains. The material at the right center is probably calcium hydroxide.



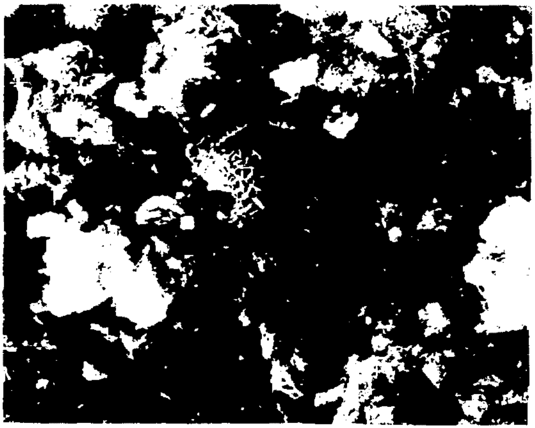
Photomicrograph 3a. Twenty-eight-day-old grout sample from Plug 1 core, Barrel 1, Box 10, X920. This is a typical and is believed due to whiskers of halite that developed during sample preparation.



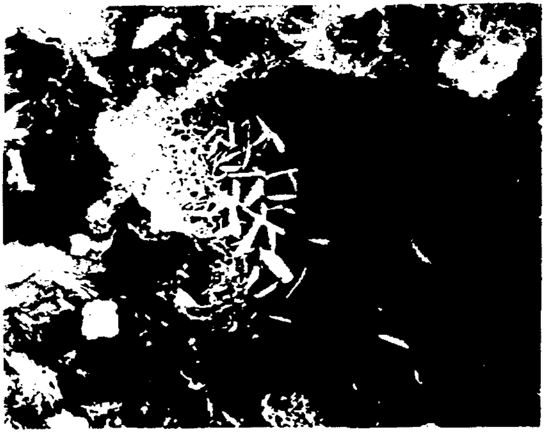
Photomicrograph 3b. Same as above but Barrel 3, Box 8, X850. Typical appearance of this material at 16- and 28-day ages. This is an intermediate magnification to those in 2a and 2b.



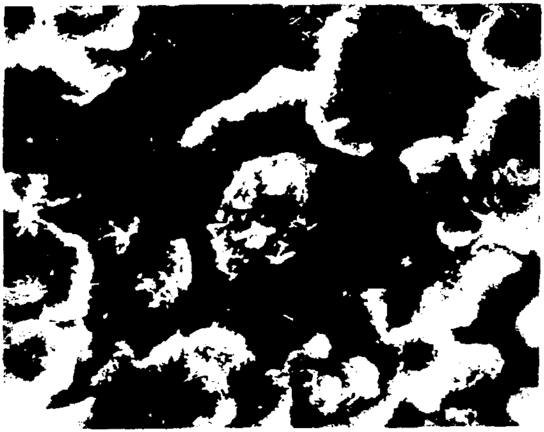
Photomicrograph 4a. Twenty-eight-day-old grout from control cylinder for Plug 3, X190. Several air voids are evident.



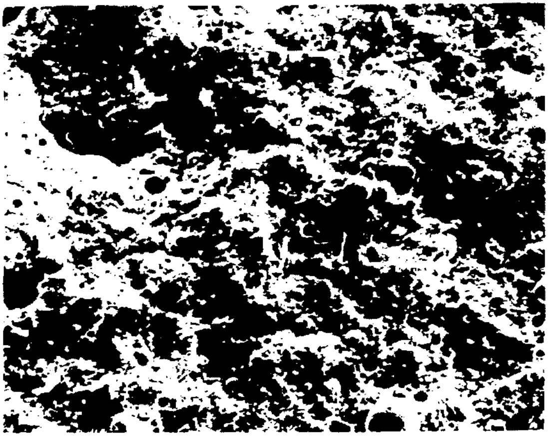
Photomicrograph 4b. An area of 4a at X1900. Note the porous appearance.



Photomicrograph 5a. Same as 4b at X4750. The tabular crystals may be calcium monochloroaluminate hydrate.



Photomicrograph 5b. Thirty-one-day-old grout sample from recirculated return cylinder 6, X1920.



Photomicrograph 6a. Twenty-eight-day-old normal consistency Type I portland cement paste with 30 percent flyash, X200. Compare this dense paste with the porous appearance of the grout in 1a, 2a, and 4a.

Photomicrograph 6b. A portion of 6a at X2000. Compare with 2b, 4b, and 5b.

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

IN REPLY REFER TO WESCI

28 April 1978

MEMORANDUM THRU: C/ENGINEERING SCIENCES DIVISION
C/ENGINEERING MECHANICS DIVISION
C/STRUCTURES LABORATORY

FOR: R. A. BENDINELLI, C/GROUTING BRANCH, STRUCTURES LABORATORY

SUBJECT: Effect of Salt-Free or Salt-Saturated Mixing Water on Embedded Salt Cores

1. Short lengths of nominal 4-in. diameter salt cores were cast in grout cylinders to determine the effect of salt-free and salt-saturated mixing water on the salt cores.

2. Photographs 1 through 3* show that when the mixing water is fresh it dissolves some of the salt core leaving an open volume along the interface of the grout and the salt. Conversely, when the mixing water is already salt-saturated a tight contact between the salt and the grout is maintained. Therefore, salt-saturated mixing water should be used if grout is used to plug holes in salt.

A. D. Buck

A. D. BUCK
Chief, Petrography
and X-ray Branch

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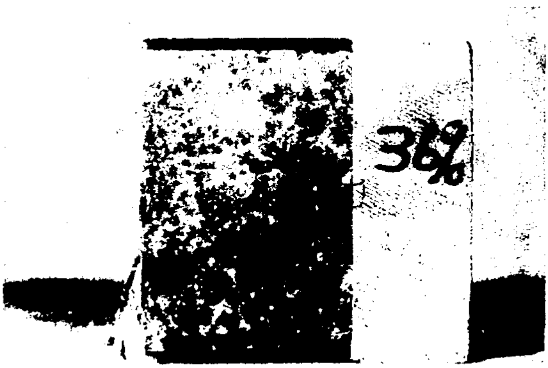
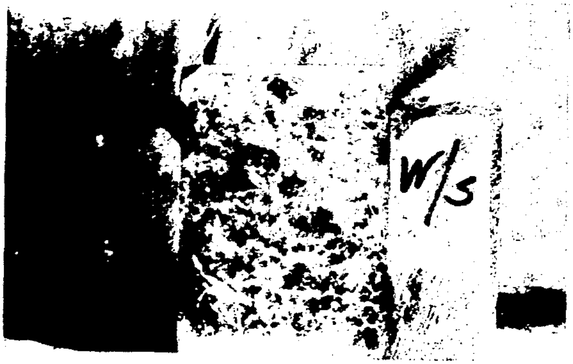
* The surfaces shown were produced by sawing using oil to cool the saw and remove cuttings



Sawed surfaces of salt cores embedded in grout containing 0 and 36% salt in the mixing water, respectively. Specimens were cut after a push out test was made. The dissolving effect of the nonsaturated water on the salt core is apparent.



Sawed surfaces of salt cores cast in grout containing 0 and 36% salt in the mixing water, respectively. The dissolving effect of the nonsaturated water on the salt core is apparent.

The salt core in the upper part of Photograph 2 removed from the grout to show that the nonsaturated mixing water in the grout dissolved some of the salt so there was no bond remaining.

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

IN REPLY REFER TO WESCI

5 July 1978

MEMORANDUM FOR: CHIEF, GROUTING BRANCH, STRUCTURES LABORATORY

SUBJECT: X-Ray Diffraction Examination of Five Cements

1. All of the cements were examined in their as received condition. They are identified below:

Structures Laboratory Serial No.	Description
No serial No.	Chem-Stress II (75) cement from Southwestern Portland Cement Co., Victorville, Calif.
RC-793	A newer sample of Chem-Stress II cement from the same plant as above.
RC-762	El Toro Chem-Comp cement from Southwestern Portland Cement Co., El Paso, Texas.
RC-785	Oil well Class "H" cement from Southwestern Portland Cement Co., El Paso, Texas.
RC-800	El Toro 35 Class "C" cement from Southwestern Portland Cement Co., Odessa, Texas. This is said to be like a Type III.

2. Both samples of Chem-Stress II cement were received through the Dowell Co. at the Nevada Test Site.

3. None of the five cements contained detectable crystalline tricalcium aluminate (C_3A) or a substituted form of C_3A.

4. The Class "H" cement (RC-785) contained alite (C_3S), belite (C_2S), calcium aluminoferrite, gypsum, anhydrite, and possibly a small amount of calcite. There was more alite than belite and more anhydrite than gypsum.

5. The Class "C" cement (RC-800) contained alite, calcium aluminoferrite, anhydrite, and possibly a little magnesia (MgO). In addition to the lack of detectable C_3A there was no definitely detectable belite. This dominance of alite over belite is common in a cement said to be like a Type III.

WESCI 5 July 1978
SUBJECT: X-Ray Diffraction Examination of Five Cements

6. The compositions of the other three cements were compared. The results are shown in Table I. The Chem-Stress II (75) sample was the most hydrated and the other Chem-Stress II sample (RC-793) was the least hydrated of the three, but all of them showed some hydration.

1 Incl
Table

A. D. BUCK
Chief, Petrography and X-Ray Branch
Structures Laboratory

Table 1

Composition and Relative Amounts of Compounds*

in Three Expansive Cements

Constituents	Chem-Stress II (75) Cement	Chem-Stress II (RC-793)	El Toro Chem-Comp (RC-762)
Portland cement			
Alite	3	1	1
Belite	1	1	1
Calcium alumino-ferrite	2	2	1
C_3A		←not detected→	
Hydrated compounds			
Calcium hydroxide	1	1	3
Ettringite	1	not detected	1
Expansive constituents			
Anhydrite	1	1	3
Hemihydrate	?**	not detected	not detected
Gypsum	1	not detected	not detected
$C_4A_3\overline{S}$	1	3	2
CaO	?**	1	2
MgO	1	1	3

* The numbers indicate relative amounts of a constituent between cements with one being most and three least.

** A question mark indicates a tentative identification.

APPENDIX C

Dowell Laboratory Memorandum

DOWELL DIVISION OF DOW CHEMICAL U.S.A.

Tulsa, Oklahoma
November 18, 1977

E. F. Shumaker
Midtex

c:
D. L. Free, Tulsa

Ed, the included lab data was conducted on cement samples obtained from Sandia - ERDA well number 10 which was cemented 10-1-77. We received three samples; one core sample from downhole and two surface samples labeled plug 1 and plug 2.

The surface sample and the drilled core sample were found to be very similiar in the tests. The surface sample when analysed by the SEM had the cubic salt structure throughout its porosity. The drilled sample had a more glazed appearance. There were other slight variations in permeability and degree of hydration.

Lloyd B. Spangle

/sf

Attachments

Lab Data

Reference:

Sandia - ERDA well number 10 cemented 10-1-77 (4000 ft, 128°F BHST)

Cement System Used:

70:30 Incor C:Litepoz 3 + 2% salt gel + 5#D30/sk + 30% D44 + 2% D33 + 0.1% D45 mixed at 14.7 lb/gal.

Test Samples:

Set samples of the cement system were drilled from the well bore. Also samples were collected at the surface directly from the mixing tub. These samples were submitted for analysis as follows:

Density

Sample	g/cc	lb/gal
Drilled core	1.710	14.25
Surface cement #2	1.689	14.08

Permeability

This test is described in API RP10B section 9. A cement permeameter was used to measure permeability to "brine" in this test.

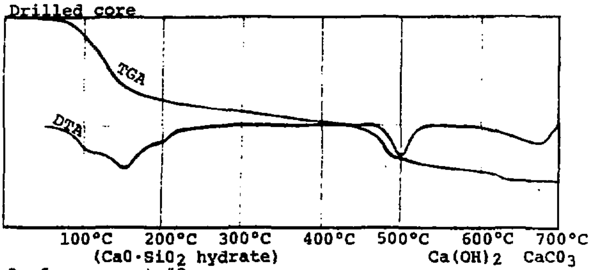
Sample	Flow Rate	ΔP	K
Drilled core	0.00067 ml/sec	100 psi	0.046 md
Surface cement #2	0.000046 ml/sec	100 psi	0.0035 md

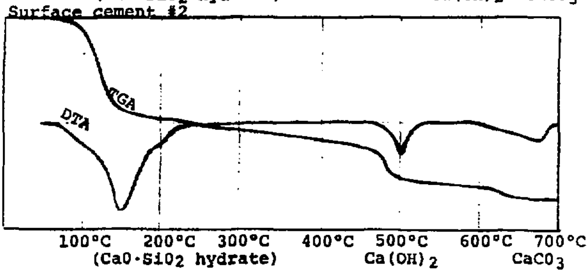
Compressive Strength

Sample	Force	Area	PSI
Drilled core	1850	0.78 $in.^2$	2370
Surface cement #2	1250	0.78 in^2	1600

Differential & Thermogravimetric Analysis

(Simulated Thermograms)

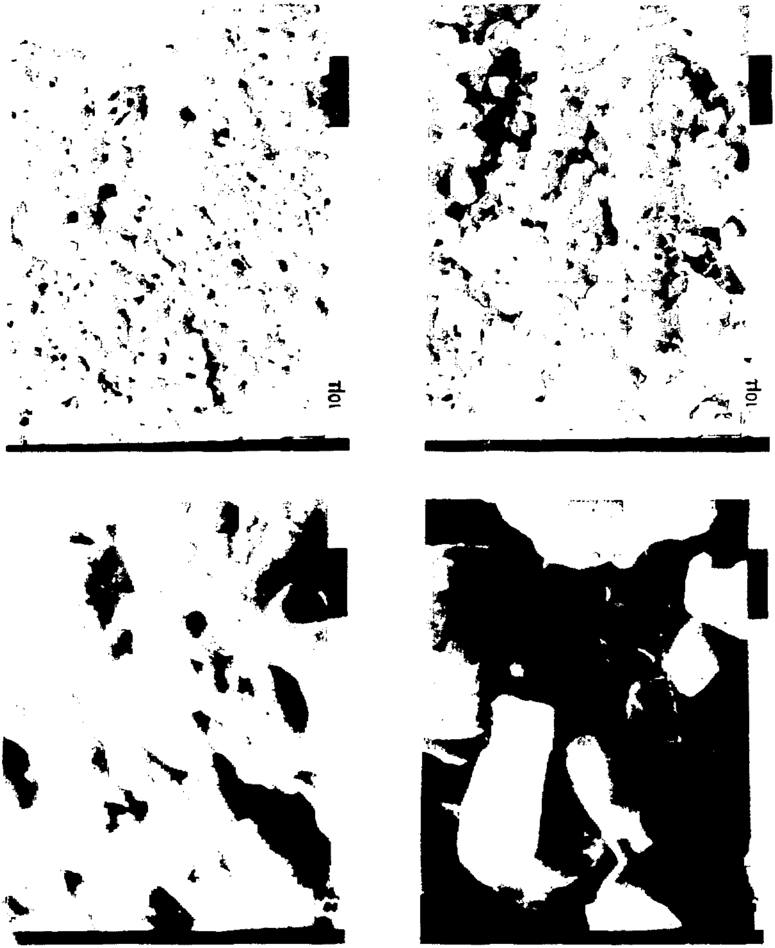




TGA Weight Loss:		Percent of Total Wt.
Drilled core	$CaO \cdot SiO_2 - H_2O$	= 13.7
	$CaO \cdot -H_2O$	= 2.7
	$CaO \cdot -CO_2$	= 0.8
Surface cement	$CaO \cdot SiO_2 - H_2O$	= 17.5
	$CaO - H_2O$	= 3.0
	$CaO - CO_2$	= 0.5

Scanning Electron Microscope

Drilled Core Surface Cement #2



X-Ray Diffraction Analysis

Sample	Low(<15%)
Drilled core	Calcium silicate hydrate gel Portlandite Halite
Surface cement #2	Portlandite Halite

Optical Emission Spectrographic Analysis

Sample	Major	Minor
Drilled core	Calcium	Magnesium, Silicon, Aluminum, Iron, Sodium
Surface cement #2	Calcium	Magnesium, Silicon, Aluminum, Iron, Sodium

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