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**Cement Technology for Plugging Boreholes
in Radioactive Waste Repository Sites:
Progress Report for the Period October 1, 1977,
to September 30, 1978**

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CHEMICAL TECHNOLOGY DIVISION

NUCLEAR FUEL AND WASTE PROGRAMS

Cement Technology for Borehole Plugging
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CEMENT TECHNOLOGY FOR PLUGGING BOREHOLES IN RADIOACTIVE
WASTE REPOSITORY SITES: PROGRESS REPORT FOR THE
PERIOD OCTOBER 1, 1977, TO SEPTEMBER 30, 1978

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Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

CONTENTS

	<u>Page</u>
PREFACE.....	v
SUMMARY.....	1
1. INTRODUCTION.....	3
2. EXPERIMENTAL PROCEDURES AND RESULTS.....	4
2.1 Mix Ingredients.....	4
2.2 Properties of the Wet Mix.....	15
2.2.1 Set time and slump.....	15
2.2.2 Bleeding characteristics.....	19
2.3 Properties of the Cementitious Solids.....	19
2.3.1 Moisture, density, and porosity measurements.....	21
2.3.2 Compressive strength.....	27
2.3.3 Thermal conductivity.....	40
2.3.4 Permeability.....	50
2.3.5 Shrinkage characteristics.....	56
2.4 Data Acquisition and Analysis.....	61
3. FUTURE STUDIES.....	63
4. ACKNOWLEDGMENTS.....	63
5. REFERENCES.....	64
6. APPENDIX: RESEARCH PLAN FOR "CEMENT TECHNOLOGY FOR BOREHOLE PLUGGING" SUPPORTED BY THE OFFICE OF NUCLEAR WASTE ISOLATION.....	67

PREFACE

This is the first in a series of annual progress reports summarizing the research and development efforts on cement technology relative to borehole plugging. The work was conducted in the Chemical Technology Division of the Oak Ridge National Laboratory (ORNL) during the period October 1, 1977, to September 30, 1978. Previous work in this field has been described in the following progress reports issued by the Office of Waste Isolation:

1. National Waste Terminal Storage Program Progress Report for the Period October 1, 1976 to September 30, 1977, Y/OWI-9 (April 1978).
2. National Waste Terminal Storage Program Progress Report for the Period April 1, 1975 to September 30, 1976, Y/OWI-8 (Nov. 30, 1976).

CEMENT TECHNOLOGY FOR PLUGGING BOREHOLES IN RADIOACTIVE WASTE
REPOSITORY SITES: PROGRESS REPORT FOR THE PERIOD
OCTOBER 1, 1977, TO SEPTEMBER 30, 1978

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SUMMARY

In the selection of a site for use as a permanent radioactive waste repository, provision must be made to seal all holes drilled in the area to ensure the integrity of the site. This program was initiated to develop and test cementitious mixtures suitable for plugging such holes. Experiments are now in progress using 34 batches of cements from 13 different locales, representing 11 types of cement, and 17 batches of fly ash from 14 suppliers. Data are being obtained from physical and chemical test methods and from measurements made in parametric studies involving cement--fly-ash concretes and saltcretes.

Wet-mix studies have revealed that the addition of 10 wt % salt to a standard mortar will double the initial and final set times. Results show that the set time of the saltcrete can be increased or decreased by the addition of a lignite fly ash or a bituminous fly ash respectively.

Procedures were established for vacuum drying cementitious specimens to remove unbound water without causing damage. Drying is required for porosity determinations as well as certain thermal conductivity and permeability measurements. Three methods were used to determine the initial porosities of selected specimens: saturated and dry densities, helium pycnometry, and mercury intrusion. Further studies must be made to determine which of these procedures is most advantageous.

The compressive strengths of solids were measured via newly developed procedures with precisions ranging from ± 2 to $\pm 8\%$. Mathematical expressions derived from the results of measurements on mortars gave the strength at 7, 28, and 91 days as a function of the weight percent sand in the mortar.

The compressive strengths of cement--fly-ash concretes were found to vary with curing time and to depend on the composition of the fly ash. The strengths of saltcretes decreased with increasing salt concentration but increased with the addition of fly ash; the effect of the fly ash composition was apparently negligible.

The thermal conductivities of cementitious solids, as measured by a Dynatech TCFM-20 instrument, were found to increase with density and with sand and/or salt concentration. Measurements made over a temperature

range of 30 to 300°C showed that the thermal conductivities of saltcretes decreased with increasing temperature but remained almost constant in neat cement pastes. The conductivity values ranged from 0.4 W/m·K for a neat cement paste to 1.8 W/m·K for a saltcrete.

Gas and liquid permeability measurements are in progress using a Hassler cell procedure. Although gas measurements are dependent on the degree of drying experienced by the specimen, they can be used to detect microcracking and to calculate the apparent liquid permeability of the specimen. Results obtained for a number of saltcretes under the same drying conditions showed that the apparent liquid permeability decreased with increasing salt content. For example, it varied from 6×10^{-7} for 0 wt % salt to 1.25×10^{-8} darcy for a saltcrete containing 63.2 wt % salt. Initial liquid permeability measurements on concretes gave values about two orders of magnitude less than those calculated from gas measurements.

The standard ASTM procedure was used to measure the shrinkage of cementitious solids after an initial 24-hr curing period. In general, the shrinkage of neat pastes and saltcretes varied approximately linearly with time, while cement--fly-ash solids showed a high rate in the first few weeks followed by a lower rate for a longer time period. The reproducibility of these measurements was very poor; therefore, additional studies will be required to improve the reliability of the data and to assess the significance of the shrinkage results.

The DASAVOR computer program, which was used for the storage and collation of data generated in this investigation, has been revised to increase its capabilities.

1. INTRODUCTION

In the selection of a site for a permanent repository for radioactive wastes, provision must be made for plugging all holes drilled in the area in order to ensure the integrity of the site. These plugs must form leak-proof bonds with the wall rock and have lifetimes comparable to the surrounding rock formations. An evaluation of previous work indicated that one of the more viable solutions involves the use of cementitious materials.¹

The Cement Technology for Borehole Plugging Program was established to assist the Office of Waste Isolation (now the Office of Nuclear Waste Isolation) in devising and testing cementitious mixtures suitable for plugging drill holes that may represent a hazard to a radioactive waste repository. These openings may range in size from small exploratory holes to mine shafts. The primary characteristics that the plug solids must demonstrate are high density, low permeability, and long-term durability.

The dominant theme throughout this program has been one of quality assurance, that is, the reliability of the physical and chemical measurements and the quality control measures exercised with respect to ingredients used to make the plug material. Thus, the major emphasis has been on the development of suitable methods for measuring the physical and chemical properties of cementitious solids and aggregates.

During this report period, systematic studies were started on pozzolanic (fly ash)--cement and salt-cement mixtures. Many of the monuments, bridges, etc., built during the time of the Roman emperors still stand as a tribute to the durability and permanence of these types of cementitious mixtures.² Fly ash serves as an excellent pozzolan and, in fact, offers some advantages over natural pozzolans.³ Moreover, discussions with prominent cement technologists in this country have indicated that the program's objectives can probably be achieved by investigating the characteristics of pozzolanic cements; in addition, such studies could significantly advance the state of the art in concrete research.

Salt-cement mixtures or saltcretes have been widely used in the oil well cement industry to ensure good bonding between the grouts and the

sections of salt or shale encountered in the wall of a hole. The addition of salt to a cement slurry used in oil wells penetrating a salt formation is necessary to prevent solubilization of the latter. In the case of clays and shales, the additional salt helps to prevent such sections from becoming soft and/or sloughing off during the plugging operation.⁴⁻⁸

In this report, data are presented from parametric studies that are in progress to determine the effects of salt and various pozzolans on the properties of mortars, saltcretes, and cement-pozzolan concretes. These data were obtained from tests covering all stages of the p. mixtures, including analyses of the mix ingredients and properties of the wet mix and the cured solid.

2. EXPERIMENTAL PROCEDURES AND RESULTS

The studies made during this report period emphasized methods and procedures for accurately measuring the physical properties of cementitious grouts and the resulting solids after appropriate curing times. The test methods used for these determinations were developed primarily by modifying existing procedures to meet the requirements of this investigation. The procedures used and the results obtained thus far are discussed in the various subsections that follow.

2.1 Mix Ingredients

We are using a wide variety of cements and fly ashes in the investigations now in progress. Multiple batches of several different types of cement and fly ash have been procured from selected areas throughout the United States. The variations observed in these samples and the effects produced on the resulting solids should be helpful in determining the degree of quality assurance that must be maintained on the mix ingredients to meet the final solid product specifications. Currently, 34 batches of cement, representing 11 cement types and obtained from 13 different locations, are available for testing. In addition 17 batches of fly ash, representing 14 locations (Fig. 1 and Table 1), are being used.

Prior to testing, all cements and fly ashes are analyzed according to the ASTM standard procedure⁹ by the ORNL Analytical Chemistry Division.

Fig. 1. Sources of cements and fly ashes under investigation. (For description of materials and supplies, refer to Table 1.)

Table 1. Sources of cements and fly ashes

Number ^a	Supplier	City and state	Map location
C-1	Santee Cement Co.	Holly Hill, S.C.	S
C-2			
C-3	Universal Atlas Cement Co., Division of U.S. Steel	Birmingham, Ala.	E O
C-4			
C-5	Universal Atlas Cement Co.	Waco, Tex.	R
C-7	Marquette Cement Mfg. Co.	Memphis, Tenn.	N
C-8	Lone Star Industries, Inc., Central Research Laboratory	Houston, Tex.	I
C-9			
C-10	Marquette Cement Mfg. Co.	Memphis, Tenn.	N
C-11	Trinity Division of General Portland	Dallas, Tex.	H
C-12			
C-13			
C-14	Southwestern Cement Co.	El Paso, Tex.	R
C-15	Marquette Cement Mfg. Co.	Memphis, Tenn.	N
C-16	Peerless Cement Co.	Detroit, Mich.	K
C-17			
C-18			
C-19	Carolina Giant Cement Co.	Harleyville, S.C.	S
C-20			
C-21 ^b			
C-22			
C-23	Southwestern Portland Cement Co.	Odessa, Tex.	R
C-24	Southwestern Portland Cement Co.	Victorville, Calif.	B

Table 1 (continued)

Number ^a	Supplier	City and state	Map location
C-25	Marquette Cement Mfg. Co.	Memphis, Tenn.	N
C-26			
C-27			
C-28			
C-29 ^b			
C-30			
C-31 ^b	Lone Star Industries, Inc.	Maryneal, Tex.	H
C-32			
C-33			
P-1	Appalachian Power Co., Div. of American Electric Co.	Charleston, W. Va.	L
P-2	U.S. Army Corps of Engineers, Waterways Experiment Station	Vicksburg, Miss.	P
P-3	Amax Resource Recovery Systems, Inc.	Atlanta, Ga.	Q
P-4	Tennessee Valley Authority	Kingston, Tenn.	M
P-5	Northern States Power Co.	St. Paul, Minneapolis, Minn.	I
P-6	Trinity Division of General Portland Cement Co.	Dallas, Tex.	H
P-7	Tennessee Valley Authority	Kingston, Tenn.	M
P-8	Comanche Power Plant	Pueblo, Colo.	F
P-9	Basin Electric Coop.	Velma, N.D.	D
P-10	Big Stone Plant	Big Stone, S.D.	T
P-11	Otter Tail Power Co., Hoot Lake Plant	Fergus Falls, Minn.	I
P-12	Saskatchewan Power Corp.	Grand Fork, N.D.	D

Table 1 (continued)

Number ^a	Supplier	City and state	Map location
P-13	Pozzolanic Northwest, Inc.	Kent, Wash.	A
P-14	Mineral Specialties, Inc.	Billings, Mont.	C
P-15	Tennessee Valley Authority,	Kingston, Tenn.	M
P-16	Haliburton Services, Inc.	Duncan, Okla.	E
P-17	Dowell Pozzolan	Artesia, N. Mex.	G

^aC refers to cement; P refers to fly ash or natural pozzolan.

^bHas not been analyzed or tested.

Periodically, an aliquot from a large sample of Type I Portland cement is resubmitted as a control to check the precision of the analytical techniques and the analysts (Table 2). The results have been quite acceptable in most cases. After seven complete analyses had been made on the same batch of cement, the standard deviations for eight of the constituents were less than $\pm 15\%$. The exceptions were TiO_2 ($\pm 16.5\%$), MgO ($\pm 23\%$), P_2O_5 ($\pm 49\%$), and Na_2O ($\pm 100\%$).

Analytical data are now available on 25 of the 34 batches of cement, including 9 different batches of Type I and 4 batches of Type II Portland cement (Table 3). Large variations were observed in the concentrations of some of the constituents of the various batches of Types I and II cement; however, they were still within the limits set by ASTM^{*} for the particular type of cement. No significant variations have been observed in the test data obtained with the different Type I cements that can be traced to the variations in the composition of the cement.

Analytical evaluations of all of the fly-ash specimens were also made (Table 4). These samples include both class F and class C fly ashes. Class F fly ash, which is produced by burning bituminous coal, is composed primarily of silica, alumina, and ferric oxide, with only small amounts of sodium, potassium, magnesium, lime, and sulfate. Class C fly ash, which is obtained from lignites, contains much higher percentages of lime, alkalies, sulfate, and magnesia. As would be expected, these differences lead to wide variations in physical properties when the fly ashes are incorporated in cementitious solids (see Sect. 3).

The surface area and the average particle size were determined for the cements (Table 3) as well as the fly ashes (Table 4). Particle size distribution curves were obtained on all ingredients of the mix. The values obtained for the two types of cement, class H and class C, that have been proposed for use in the 1979 Borehole Plugging test¹⁰ are shown in Figs. 2 and 3 respectively. As was known, class H cement is a much coarser grind than class C. A complete evaluation of these cements will be made during the next report period.

* ASTM = American Society for Testing and Materials.

Table 2. Control analyses (wt %) of Type I Portland cement^a

	LOI ^b	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	MgO	SO ₃	P ₂ O ₅	Na ₂ O	K ₂ O	Free calcium
	1.75	20.05	2.39	5.65	0.31	62.0	4.27	2.73	0.065	0.32	0.12	0.73
	1.68	20.60	2.62	6.15	0.31	59.6	5.39	2.61	0.059	0.49	0.15	0.76
	1.75	20.09	2.70	4.35	0.30	64.0	3.29	2.57	0.056	0.11	0.16	0.75
	1.67	20.2	2.56	4.27	0.32	63.65	3.35	2.56	0.16	0.080	0.125	0.53
	1.71	20.3	2.46	4.37	0.35	63.82	3.45	2.54	0.15	0.079	0.147	0.68
	1.70	20.51	2.52	4.79	0.27	64.5	3.04	2.63	0.073	0.052	0.13	0.63
	1.74	19.9	2.60	4.84	0.20	64.6	3.65	2.31	0.16	0.06	0.16	0.78
Mean ($\bar{X}$)	1.71	20.24	2.55	4.92	0.29	63.17	3.80	2.56	0.103	0.17	0.14	0.69
Std. dev. (S_x)	0.033	0.25	0.10	0.72	0.05	1.79	0.88	0.13	0.05	0.17	0.02	0.089
$\frac{S_x}{\bar{X}} \times 100 = \%$	1.94	± 1.25	± 4.0	14.7	16.52	± 2.84	23.28	5.02	48.9	100	11.9	± 12.9

^aC-7 cement from Marquette Cement Mfg. Co., Memphis, Tenn.

^bLOI = loss on ignition.

Table 3. Analytical data for 25 batches of cement^a

Number ^b	Type	Surface area (m ² /g)	Density (g/cc)	Particle size ^c (μ)	SiO ₂ (Z)	CaO (Z)	Free CaO (Z)	Al ₂ O ₃ (Z)	Fe ₂ O ₃ (Z)	SO ₃ (Z)	P ₂ O ₅ (Z)	Na ₂ O (Z)	MgO (Z)	K ₂ O (Z)	TiO ₂ (Z)	LOI ^d (Z)	Moisture (Z)	lime ^e saturation factor
C-10	I	0.882	3.18	11.36	20.7	64.3	0.68	4.64	2.50	2.77	0.10	0.05	3.83	0.15	0.31	2.0	0.22	0.95
C-30		1.12	3.18	12.62	21.9	64.4	0.53	4.72	2.00	1.89	0.14	0.05	2.14	0.14	0.30	2.04	0.29	0.92
C-31		1.34	3.12	11.46	20.7	63.8	1.38	4.87	2.83	3.32	0.46	0.19	1.68	0.46	0.25	2.29	0.55	0.94
C-17		1.20	3.08	13.33	21.28	61.7	1.06	4.84	2.44	3.13	0.18	0.29	3.43	0.68	0.14	1.18	0.48	0.89
C-20					20.05	55.3	0.62	4.58	2.59	2.94	1.33	0.10	1.21	0.37	0.16	0.79	0.10	1.00
C-25					20.82	62.4	0.78	4.18	1.87	3.24	0.33	0.06	2.37	0.15	0.30	3.41	0.14	0.93
C-26					20.71	60.3	0.93	4.13	1.91	2.79	0.36	0.06	2.64	0.15	0.32	1.84	0.05	0.91
C-27		1.08	3.17	12.78	20.76	60.9		4.12	3.13	0.35	0.13	0.20	3.20	0.55	0.20	1.23	0.04	0.93
C-28		1.07	3.16	13.50	20.65	60.7		4.12	3.09	0.35	0.12	0.20	3.21	0.55	0.20	1.09	0.09	0.93
C-2	IP	1.58	2.96	6.97	26.24	53.4	0.24	10.3	3.10	3.14	0.21	0.12	0.87	0.35	0.43	2.01		
C-1	II	1.37	3.14	10.16	21.56	61.5	0.29	4.95	3.04	2.48	0.08	0.10	2.61	0.33	0.28	1.68		
C-3		0.964	3.13	13.99	21.18	64.4	1.20	4.31	3.65	2.99	0.05	0.20	1.67	0.57	0.15	1.18		
C-12		1.14	3.23	12.52	20.47	63.9	0.54	4.40	5.52	2.63	0.18	0.13	1.06	0.36	0.10	0.67	0.77	
C-19					20.86	66.4	0.16	3.93	4.00	2.63	1.26	0.09	1.23	0.27	0.16	0.79	0.11	
C-4	III	1.30	3.16	7.31	19.93	64.1		6.45	2.29	3.14	0.06	0.19	1.76	0.34	0.32	1.80		
C-16		1.68	3.13	6.17														
C-14	V	0.838	3.19	13.27	22.7	65.0	0.68	2.99	2.90	1.90	0.14	0.24	1.63	0.38	0.23	0.42		
C-11	Trinity Lite Mate	3.09	2.79	8.88	20.3	63.8	0.79	4.37	2.46	2.54	0.15	0.08	3.45	0.15	0.35	1.71		
C-13	H	0.98	3.18	42.66	20.59	64.1	0.58	4.08	6.08	2.24	0.18	0.14	1.11	0.42	0.10	1.05		
C-33		0.73	3.11	42.53	22.1	65.2	0.34	3.30	3.33	2.26	0.12	0.36	2.34	0.70	0.21	0.82	0.17	
C-32	C	1.24	3.21	7.70	21.83	64.2	0.38	2.40	4.54	3.26	0.12	0.10	1.59	0.45	0.16	0.86	0.11	
C-9		1.19	3.12	7.74	20.85	61.8	0.73	4.97	4.55	2.95	0.06	0.44	2.46	0.53	0.14	1.06		
C-6	Lumite	1.34	3.14	13.12	7.56	34.0	<0.05	44.2	8.15	1.98	0.07	0.18	0.94	0.09	1.57	1.31		
C-23	Chem Comp				19.33	61.2		4.05	2.50	5.4		0.10	0.8	0.26	0.10	1.02		
C-24	Chem Stress-II				15.32	56.8		6.16	1.52	13.4		0.14	2.1	0.41	0.73	1.77		

^aThe Ca, K, Na, Fe, Mg, and Al were analyzed on a Perkin-Elmer No. 460 Atomic Absorption Photometer. The Si was determined by a gravimetric procedure. Analytical data are given in wt %.

^bSee Table 1.

^cMaximum particle size of 50 wt % of the particles.

^dLOI = loss on ignition.

^eThe lime saturation factor was determined by the equation²⁰ $L. S. F. = \frac{(CaO) - 0.7 (SO_3)}{2.8 (SiO_2) + 1.2 (Al_2O_3) + 0.65 (Fe_2O_3)}$

Table 4. Analytical data for class F and class C fly ashes

No.	Class	Surface area (m ² /g)	Density (g/cm ³)	Particle size ^b (μ)	Moisture (%)	SiO ₂ (%)	CaO (%)	Fe ₂ O ₃ (%)	NaO (%)	P ₂ O ₅ (%)	TiO ₂ (%)	LOI (%)	MgO (%)	Al ₂ O ₃ (%)	SO ₃ (%)	K ₂ O (%)	C (%)
P-1	F	1.18	2.31	12.17	0.1	53.5	0.59	3.61	0.32	0.22	1.88	1.67	0.82	26.2	0.29	2.76	1.23
P-2	F	1.15	2.48	13.91	0.22	43.2	2.73	18.6	0.35	0.52	1.22	4.08	0.85	20.2	1.16	2.30	2.73
P-3	F	1.05	2.49	12.68	0.06	44.6	3.09	15.3	0.41	0.78	1.20	3.33	1.01	23.0	0.97	2.53	2.43
P-4	F	1.92	2.44	9.25	0.09	46.76	1.65	8.36	0.77	0.49		3.17	1.14	25.3	0.633	3.08	2.29
P-5	C	1.61	2.40	8.04	0.06	43.3	15.01	7.60	3.10	0.74		3.08	2.54	19.5	2.74	1.25	0.755
P-6	C	1.04	2.50	12.54	<0.01	41.9	19.5	4.84	0.54	0.14	1.52	2.14	3.08	14.1	1.51	0.55	0.185
P-7	F	2.69	2.45	9.65	0.07	50.2	1.90	11.95	0.39	1.16		2.63	0.98	24.5	0.33	2.91	
P-8	C	1.47	2.60	11.78	0.019	39.7	24.78	5.40	1.64	1.85		0.81	3.95	19.4	0.27	0.48	0.84
P-9	C	1.51	2.66	14.37	<0.01	40.8	27.93	5.16	1.52	0.22		0.73	7.53	12.9	0.26	0.80	2.17
P-10	C	3.56	2.79	16.84	0.01	38.8	23.07	5.78	6.47	0.15		3.26	8.12	9.58	1.25	1.02	2.66
P-11	C	0.85	2.91	15.24	0.04	31.0	27.13	9.36	5.61	0.62		0.63	8.22	13.3	0.99	0.40	0.65
P-12	C	0.35	2.37	24.85	0.09	44.6	12.89	3.76	5.85	0.43		0.89	2.88	20.8	0.32	0.60	0.91
P-13	F	0.814	2.31	13.38	0.04	44.46	7.50	6.68	3.30	13.2		0.79	1.58	22.3	0.08	0.51	0.204
P-14	C	1.30	2.49	11.72	<0.01	42.01	17.4	5.36	0.98	0.33		0.37	5.07	23.0	1.31	0.59	<0.05
P-15	F	1.34	2.36	10.94	0.09	48.57	1.32	9.00	0.33	0.99		2.84	1.31	28.5	0.37	3.14	2.70
P-16	F	3.72	2.54	11.17	0.46	44.3	7.36	19.6	0.25	0.58		5.49	0.38	16.9	3.08	2.22	2.19
P-17	C	1.71	2.62	12.36	0.03	39.4	32.5	4.36	0.76	0.901	0.88	0.93	2.67	11.8	2.28	0.44	0.29

^aAnalytical data are given in wt %.^bMaximum size of 50 wt % of the particles.

ORNL DWG 79-227

Fig. 2. Particle size distribution of type H cement.

ORNL DWG 79-226

Fig. 3. Particle size distribution of type C cement.

Particle sizes of the ingredients of the mix were determined on a Sharples Micromerograph. A small aliquot of the material in question was blown at a high velocity through an adjustable aperture into the top of a 7-ft vertical column where the dispersed particles came to terminal velocities as determined by Stokes' law. A recording servomechanical balance was used to weigh the particles collecting at the bottom of the column. The resulting weight-time curve was converted to a cumulative weight--particle size distribution curve by the application of Stokes' law.

All surface area analyses were performed on a Micromeritic Digisorb 2500 Analyzer. Calculations were made using a least-squares fit of a five-point nitrogen isotherm.

2.2 Properties of the Wet Mix

Slump, set time, and bleed characteristics are among the important properties that must be measured to determine the suitability of a mix for placement in boreholes. ASTM Procedure C305-65 reapproved 1970⁹ was used to prepare the wet mixes used in these tests. For specimens containing fly ash, the fly ash was added to the cement and the resulting mixture was then treated as the cement phase in the standard mixing procedure. In the case of saltcretes, the water was presaturated with salt, and any remaining salt was treated as if it were sand in the standard mixing procedure. The data reported for this period address the effect of salt, with and without fly ash present, on the properties of the wet mix.

2.2.1 Set time and slump

The initial and final set times of the wet mixes were determined by the Penetrometer method, ASTM Procedure C403-70,⁹ in which the force required to penetrate the mix to a depth of 1 in. is measured as a function of time. The initial and final set times, which are defined as the times required for a penetration resistance of 500 and 4000 psi, respectively, can be obtained directly from a curve of penetration resistance vs time (Fig. 4). In the case of extremely slow-setting cements, the final set time may be obtained by extrapolation using the relation

Fig. 4. Penetration resistance of a mortar vs time.

$$t = ap^b,$$

where t is the time, p is the penetration resistance, and a and b are constants determined by a fit from the initial part of the curve.

The addition of large amounts of salt to a standard mortar greatly increases the set times. For example, we found that a Type I Portland cement mortar with a sand content of 63.2 wt % and a water/cement (w/c) ratio of 0.60 had initial and final set times of 5.5 and 8.2 hr respectively. The substitution of 10 wt % sand with 10 wt % salt essentially doubled these set times (Table 5).

The effect of fly ash on the set times of saltcrete was dependent on the type as well as the amount of fly ash added to the mix. Saltcretes containing 30 wt % salt had initial and final set times of 12.5 and 16.8 hr respectively. The addition of 10 wt % fly ash from bituminous coal (Kingston fly ash) decreased the set times about 30%. Further additions of the fly ash increased the set times, but never to those observed for the original saltcrete. However, the addition of 10 wt % of a high-lime lignite fly ash (Pueblo fly ash) increased the set times by 15 to 20% (Table 6). Additional studies are in progress with other lignite ashes having different lime contents to determine the effect of this constituent on the properties of the wet mix.

The slump of a wet mix is routinely measured with an instrument known as a "K-slump Tester,"¹¹ which consists of a perforated steel tube surrounding a movable plastic measuring rod. The slump is determined by the amount of concrete that flows into the perforated tube. Although some differences were observed for the various saltcretes, they are within the precision of the instrument (Tables 5 and 6). Since the slump measurement is so inaccurate, it will probably be discontinued. Other methods will be examined to study the rheology of the wet mixes.

Table 5. Set times and slump measurements for saltcretes

Composition (wt %) ^a		Slump (in.)	Set time (hr)	
Sand	Salt		Initial	Final
63.2	0.0	7.4 ^b	5.5	8.2
53.2	10.0	9.9	11.6	16.1
33.2	30.0	9.0	12.5	16.8
0.0	63.2	6.2	10.9	14.5

^aAll mixes contained 23.0 wt % Marquette Type I Portland cement and 13.8 wt % H₂O (w/c ratio of 0.60).

^bAverage from two mixes of the same composition.

Table 6. Set times and slump measurements for saltcretes containing fly ash

Fly ash No. ^a	Composition (wt %) ^b		Slump (in.)	Set time (hr)	
	Fly ash	Sand		Initial	Final
P-15	10	23.2	9.7	8.7	11.7
P-15	20	13.2	6.7	10.5	13.9
P-15	30	3.2	9.5	9.7	13.8
P-8	10	23.2	9.0	15.4	19.4
P-8	20	13.2	9.5	20.0	25.6
P-8	30	3.2	c	19.6	24.6

^aThe P-15 refers to Kingston fly ash (a bituminous coal ash) and P-8 to Pueblo fly ash (a high-lime lignite ash). Complete analyses are given in Table 4.

^bAll mixes contained 23 wt % Marquette Type I Portland cement, 30 wt % salt, and 13.8 wt % H₂O (w/c ratio of 0.60).

^cNot available.

2.2.2 Bleeding characteristics

Bleeding is the appearance of water at the surface of concrete after placement but before solidification. It is essentially a sedimentation phenomenon. During the placement and solidification of a grout plug in a borehole, it would be desirable to keep the bleed at a minimum; thus bleed characteristics were determined for many of the mix compositions under investigation. Two measurements were made in accordance with ASTM Procedure C243-65:⁹ the bleeding capacity (the measure of water per unit volume of wet mix), and the initial bleeding rate.

Bleeding characteristics were determined for saltcretes with and without fly ash present. The replacement of part or all of the sand in a standard mortar with salt caused some increase in the bleeding capacity at the 10 and 30 wt % salt concentrations but greatly decreased the bleeding rates (Table 7). The addition of fly ash to saltcrete decreased both the bleeding capacity and the rate (Table 8). The extent depended on both the amount and the origin of fly ash. For example, Pueblo fly ash, a high-lime lignite type, was much more effective than a coal ash from the Tennessee Valley Authority's Kingston Steam Plant. Essentially no bleeding was observed for mixes containing 30 wt % Pueblo ash.

2.3 Properties of the Cementitious Solids

The grouts evaluated during this report period were allowed to solidify and cure at ambient temperature and pressure for 28 and 91 days prior to physical testing.

The physical properties studies included measurements of compressive strength, density, porosity, thermal conductivity, permeability, and shrinkage. Concentrations of sand, fly ash, and salt were varied to determine the effects of these ingredients on the physical properties. In some studies, the water/solids ratio was held constant; in others, the w/c ratio was constant.

Table 7. Bleed characteristics of saltcretes

Composition (wt %) ^a		Bleed rate	Bleed capacity
Sand	Salt	$\left(\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^2 \cdot \text{sec}} \right)$	$\left(\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^3 \text{ concrete}} \right)$
63.2	0.0	7.67×10^{-5}	1.98×10^{-2}
53.2	10.0	2.69×10^{-5}	3.00×10^{-2}
33.2	30.0	1.41×10^{-5}	2.28×10^{-2}
0.0	63.2	1.53×10^{-5}	1.28×10^{-2}

^aAll mixes contained 23.0 wt % Marquette Type I Portland cement and 13.8 wt % H₂O (w/c ratio of 0.60).

Table 8. Bleed characteristics of saltcretes containing fly ash

Fly ash No. ^a	Composition (wt %) ^b		Bleed rate	Bleed capacity
	Fly ash	Sand	$\left(\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^2 \cdot \text{sec}} \right)$	$\left(\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^3 \text{ concrete}} \right)$
P-15	10.0	23.2	1.71×10^{-5}	1.02×10^{-2}
P-15	20.0	13.2	9.83×10^{-6}	1.44×10^{-2}
P-15	30.0	3.2	2.59×10^{-6}	4.05×10^{-3}
P-8	10.0	23.2	9.43×10^{-6}	6.74×10^{-3}
P-8	20.0	13.2	2.05×10^{-6}	9.79×10^{-3}
P-8	30.0	3.2	$<7.0 \times 10^{-7}$	$<1.0 \times 10^{-4}$

^aP-15 refers to Kingston fly ash (a bituminous coal ash), while P-8 denotes Pueblo fly ash (a high-lime lignite ash). Complete analyses are given in Table 4.

^bAll mixes contained 23 wt % Marquette Type I Portland cement, 30 wt % salt, and 13.8 wt % H₂O (w/c ratio of 0.60).

2.3.1 Moisture, density, and porosity measurements

Density and porosity are important factors in the study of the characteristics of cementitious materials. These factors are known to have a strong influence on the permeability and the thermal conductivity of solids. Moisture content affects the density values determined for porous materials, and the degree of hydration of concretes may be estimated from the evaporable and nonevaporable water content. Thus it is important to have a reliable method for drying and saturating specimens being evaluated in the Borehole Plugging Program.

Drying studies showed that samples may be damaged if they are dried too rapidly. Extensive cracking was observed in some neat cement pastes and fly-ash mortars after being dried in an oven at atmospheric pressure at temperatures of 110 to 130°C. Such cracking would lead to erroneous values if the specimens were used in thermal conductivity or permeability measurements. Vacuum drying may also cause damage, if applied too rapidly, because of the freezing action of the evaporating water. Thus great care must be exercised in controlling the rate of drying, regardless of the procedure used.

Drying curves were obtained on identical samples using three different methods: drying over Drierite at ambient temperature and pressure, drying over Drierite at ambient temperature in a vacuum desiccator, and drying in an oven at 100°C under 0.01 torr vacuum (Fig. 5). Results show that vacuum and elevated temperatures are required in order to achieve complete drying in a reasonable time. Less than one-half of the free water was removed in 500 hr using Drierite at atmospheric pressure or in vacuum. In the current procedure, specimens are dried at 100°C under 0.01 torr vacuum until the weight loss is less than 0.1% per day. For mixtures in which microcracking is likely to occur (e.g., neat cement pastes containing fly ash), the specimens are first dried over Drierite at atmospheric pressure for at least a week before being vacuum-dried at 100°C.

Saturation and drying rates were found to be dependent on the composition of the specimen in question. Studies were made in which concretes were saturated by simple immersion in saturated calcium hydroxide solutions.

Fig. 5. Comparison of drying rates under three different conditions. Sample contained 23 wt % type I Portland cement, 20 wt % P-15 fly ash, 30 wt % salt, 13.2 wt % sand, and 13.8 wt % water.

Saltcretes were placed in saturated calcium hydroxide--salt solutions. Drying curves were obtained by drying the specimens at 100°C under 0.01 torr vacuum (Figs. 6-8). Effective saturation and drying required more than 100 hr for some compositions (Fig. 6). Others, such as a saltcrete containing 30 wt % salt and no fly ash, began to show surface disintegration after a few hours of immersion (Fig. 7). This surface effect was not evident in saltcretes containing 10% fly ash or 10 wt % salt.

Mortars containing sand or fly ash could be saturated or dried to near completion in short time periods, but they continued to gain or lose weight at low rates for hundreds of hours (Fig. 8). In such plots the 0 and 100% saturation levels were estimated from the curves and therefore may not represent absolute values. In addition, it must be remembered that specimens which show low rate changes over long periods of time may be simply indicating changes in hydration rather than changes in the free water content of the specimens.

In the future, specimens will be saturated with the appropriate solution under vacuum to decrease the time required and to ensure complete saturation. Each will remain immersed in the solution until it shows a daily weight change of less than 0.1%.

Saturated wet (ρ_w) and dry (ρ_d) densities were measured on mortars, cement pastes containing fly ash, and saltcretes with and without fly ash present. The porosity, ϵ , of a specimen is the difference between the saturated density and the dry density. The densities of the mixed constituents minus water in a specimen, ρ_s , were calculated by the relation

$$\rho_s = \frac{\rho_d}{1 - \epsilon}$$

for comparison with the theoretical density of the mixed constituents. The latter value was obtained by adding the sum of the densities of the individual components multiplied by their proportions in the solid in question. Of course, this value would simply be an approximation since it does not take into account the concentrations and densities of the hydrates that form.

The dry density showed little change with changes in sand concentrations of mortars containing 32.7 wt % water and 6.7 to 26.9 wt % sand

Fig. 6. Saturation and drying rates for a saltcrete containing fly ash. Samples contained 23 wt % type I Portland cement, 10 wt % P-8 fly ash, 30 wt % salt, 23.2 wt % sand, and 13.8 wt % water. The densities were 1.96 g/cm^3 dry and 2.13 g/cm^3 saturated. The porosity calculated from the densities was 16.8%. The weight after vacuum impregnation following drying was the same as that after the 250-hr immersion.

Fig. 7. Saturation and drying rates for a saltcrete. Sample contained 23 wt % type I Portland cement, 30 wt % salt, 33 wt % sand, and 13.8 wt % water. The densities were 1.88 g/cm³ dry, 2.07 g/cm³ saturated by immersion, and 2.08 g/cm³ saturated by vacuum impregnation after drying. The porosity calculated from the densities was 19.6% after immersion and 20.5% after vacuum impregnation.

Fig. 8. Saturation and drying rates for a standard mortar. Sample contained 23 wt % type I Portland cement, 63.2 wt % sand, and 13.8 wt % water. The densities were 2.04 g/cm³ dry and 2.24 g/cm³ saturated. The porosity calculated from the densities was 19.5%. The weight after vacuum impregnation (following drying) was the same as that after the 500-hr immersion.

(Table 9). Although mortars containing 63.2 wt % sand had much higher densities, they contained only 13.8 wt % water. The higher value agrees with the average density determined for saltcretes having a similar water concentration (Table 10).

Densities of saltcretes both with and without sand and/or fly ash are shown in Table 10. The density of the saltcrete with the highest salt content, 63.2%, is lower than the values determined for the other compositions. This can be attributed to the lower density of salt (2.16 g/cm^3) as compared with that of cement (3.2 g/cm^3) or sand (2.6 g/cm^3).

The densities of neat pastes containing various concentrations and types of fly ash decreased as the fly ash concentration increased, showing some variation with the type used (Table 11 and Fig. 9). The porosity appeared to decrease both with increasing density and with decreasing fly ash concentration; however, the change measured in each case was small (0.49 to 0.43%), and the precision of the measurement is not known at this time.

The porosities of a large number of concretes determined by the difference in saturated and dry densities are plotted as a function of density in Fig. 10. As would be expected, the porosity decreases with increasing density. Studies are now in progress to determine the porosities of concretes via mercury intrusion and helium pycnometry. Known standards will be used to determine the precision of each method, and a procedure will be established for future routine measurements.

2.3.2 Compressive strength

Compressive strength measurements were made by crushing standard 2-in. cubes that had been prepared according to ASTM procedure C-109⁹ and placed in a humidity cabinet (>90% relative humidity and 28°C) to solidify. After 24 hr, the cubes were removed from the molds and immediately wrapped twice with Parafilm M, a water-impermeable membrane. Prior laboratory studies had demonstrated that the wrapping procedure prevented the gain or loss of water. Thus the specimens were cured in the presence of only the water used in the initial mix.

Table 9. Densities of standard mortars

Cement ^a (wt %)	Composition		Cure time (days)	Saturated density, ^b ρ_w (g/cm ³)	Dry density, ρ_d (g/cm ³)	Porosity, ^b ϵ	Density of the mixed solid components ^b (g/cm ³)	
	Sand (wt %)	Water (wt %)					Measured ^c	Theoretical ^d
47.1	20.2	32.7	91	1.94	1.50	0.44	2.7	2.4-3.2
53.9	13.4	32.7	91		1.55			
60.6	6.7	32.7	28		1.55			
40.4	26.9	32.7	91	1.99	1.56	0.43	2.7	2.3-3.0
40.4	26.9	32.7	28		1.56			
53.9	13.4	32.7	28		1.57			
47.1	20.2	32.7	28		1.58			
23.0	63.2	13.8	91	2.18	1.99	0.19	2.5	2.5-2.8
23.0	63.2	13.8	28	2.19	2.00	0.19	2.5	2.5-2.8

^aAll mixes were made with Marquette Type I Portland cement.

^bValues are omitted where the saturated density has not been measured.

^cSolid density = $\rho_d / (1 - \epsilon)$.

^dThe approximate theoretical density was calculated both with and without the total water added. The solid density, which includes the water of crystallization but not the excess water, should fall in this range. The following densities were used in the calculation: fly ash = 2.45 g/cm³, sand = 2.6 g/cm³, salt = 2.16 g/cm³, cement = 3.2 g/cm³, and water = 1 g/cm³.

Table 10. Densities of saltcretes containing sand and fly ash

Fly ash type ^b	Composition ^a (wt %)			Cure time (days)	Saturated density, ρ_w (g/cm ³)	Dry density, ρ_d (g/cm ³)	Porosity, ϵ	Density of the mixed solid components (g/cm ³)	
	Fly ash	Sand	Salt					Measured ^c	Theoretical ^d
P-15	0.0	0.0	63.2	28	1.87	1.67	0.196	2.1	2.2
			63.2	91	1.87	1.67	0.200	2.1	2.2
		33.2	30.0	91	2.00	1.93	0.067	2.1	2.4
		33.2	30.0	28	2.06	1.93	0.131	2.2	2.4
	30.0	3.2	30.0	91	2.16	1.95	0.211	2.5	2.3
P-15	0.0	53.2	10.0	91	2.13	1.96	0.172	2.4	2.5
	20.0	13.2	30.0	91	2.07	1.96	0.108	2.2	2.4
P-8	30.0	3.2	30.0	28	----	1.98	-----	---	---
P-8	10.0	23.2	30.0	91	2.13	1.99	0.139	2.3	2.4
	0.0	63.2	0.0	91	2.18	1.99	0.192	2.5	2.5
		63.2		28	2.19	2.00	0.188	2.5	2.5
		53.2	10.0	28	2.22	2.04	0.180	2.5	2.5

^aAll mixes contained 23.0 wt % Marquette Type I Portland cement and 13.8 wt % water (w/c ratio = 0.60).

^bSee Table 4.

^cSolid density = $\rho_d / (1 - \epsilon)$.

^dThe approximate theoretical density was calculated using the following densities: fly ash = 2.45 g/cm³, sand = 2.6 g/cm³, salt = 2.16 g/cm³, cement = 3.2 g/cm³, and water = 1 g/cm³. Since the total amount of water added was small, it may approximate the water of crystallization.

Table 11. Densities of cement pastes containing fly ash

Cement (wt %)	Composition ^a		Cure time (days)	Saturated density, ^c ρ_w (g/cm ³)	Dry density, ρ_d (g/cm ³)	Porosity, ^c ϵ	Density of the mixed solid components ^c (g/cm ³)	
	Number ^b	Fly ash (wt %)					Measured ^d	Theoretical ^e
40.4	P-1	26.9	28		1.38			
40.4	P-5	26.9	91	1.89	1.40	0.49	2.8	2.3-2.9
53.9	P-1	13.4	28		1.42			
40.4	P-5	26.9	28		1.43			
47.1	P-5	20.2	91	1.94	1.45	0.49	2.8	2.3-3.0
60.6	P-1	6.7	28		1.45			
47.1	P-5	20.2	28		1.47			
53.9	P-5	13.4	91	1.96	1.48	0.48	2.8	2.4-3.1
53.9	P-5	13.4	28		1.49			
60.6	P-7	6.7	28	1.98	1.53	0.45	2.8	2.4-3.1
60.6	P-5	6.7	91	1.97	1.54	0.43	2.7	2.4-3.1
60.6	P-7	6.7	91	1.99	1.55	0.44	2.8	2.4-3.1

^aAll cement used was Marquette Type I. All mixes contained 32.7 wt % of water.

^bSee Table 4.

^cValues were omitted where the saturated density was not measured.

^dSolid density = $\rho_d / (1 - \epsilon)$.

^eThe approximate theoretical density was calculated both with and without the total water added. The solid density, which includes the water of crystallization but not the excess water, should fall in this range. The following densities were used in the calculations: fly ash = 2.45 g/cm³, sand = 2.6 g/cm³, salt = 2.16 g/cm³, cement = 3.2 g/cm³, and water = 1 g/cm³.

Fig. 9. Densities of cement pastes as a function of fly-ash concentrations.

ORNL DWG 79-236R

Fig. 10. Porosities of concretes as a function of density.

After being cured for the desired length of time at ambient temperature and pressure, the cubes were unwrapped, visually inspected, weighed, and measured. If discrepancies were noted in the size, shape, or weight in the individual cubes (six were crushed for each measurement), the batch was discarded and a new set prepared. The standard deviations obtained in these measurements ranged from 2 to 3% for specimens cured 7 days and from 6 to 8% for 28- and 91-day-cured cubes.

Tensile strength measurements were attempted on a number of specimens using the dog bone procedure, ASTM C190-72;⁹ unfortunately, the resulting data were so erratic that they were discarded. It was discovered that the low-range gauge could not be calibrated accurately because of flaws in the Forney LT-30 Compressive Strength Tester. (However, these flaws do not affect the higher ranges.) A Tinius Olsen machine has been ordered and should become operational during the early part of CY 1979. It will be used for making compressive and tensile strength determinations in the future.

Compressive strength measurements were made on mortars containing various concentrations of sand, neat cement pastes containing different fly ashes, and saltcretes with and without fly ash present. The values determined for the mortars served as reference points for the fly-ash and saltcrete parametric studies. The mortars, which had a water/cement + fly ash $[w/(c+f)]$ ratio of 0.485, were made with Type I Portland cement in which 0 to 40% of the cement had been replaced by sand. Measurements were made after 7, 28, and 91 days of curing. As expected, the compressive strength increased with curing time but decreased with increasing w/c ratio accompanying the increasing sand concentration (Figs. 11 and 12). The compressive strength varied as follows:

7-day curing	$Y = 24.7 - 0.48X,$
28-day curing	$Y = 39.8 - 0.794X,$
91-day curing	$Y = 45.3 - 0.47X,$

where Y is the compressive strength in MPa and X is the wt % sand present in the mortar.

Fig. 11. Compressive strengths of mortars as a function of sand content.

Fig. 12. Compressive strengths of mortars as a function of curing time.

The compressive strengths of neat cement pastes prepared with Type I Portland cement, 6.7 wt % fly ash, and a w/(c+f) ratio of 0.485 were found to depend on curing time and the fly-ash composition. After a 91-day-curing period, the compressive strength of pastes containing various fly ashes varied as follows: Kingston fly ash < Cencron fly ash < Pueblo fly ash (Fig. 13).

The most obvious difference in the compositions of the three fly ashes was the CaO content (Table 4). The lime contents of Kingston, Cencron, and Pueblo fly ash were 1.32, 15.01, and 24.8 wt % respectively. The Cencron and Pueblo material contained sufficient lime to form a cementitious solid simply by adding water. Further studies will be made during the next report period to determine the effect of the lime content on fly-ash--cement mixtures.

The strength data from studies on the effect of fly-ash concentration in pastes made with Cencron or Kingston fly ash were quite erratic, except in the case of the short-cured specimens. For 7-day-cured specimens, the compressive strength varied as follows:

$$\text{Kingston fly ash} \quad Y = 24.3 - 0.474X,$$

$$\text{Cencron fly ash} \quad Y = 31.85 - 0.488X,$$

where Y is the compressive strength in MPa and X is the wt % of the fly ash in question (Fig. 14). The decreasing strength shown with increased fly-ash additions may be attributed to the increasing w/c ratio, as was the case with the mortars. In the following studies, specimens were examined in which the w/c ratio was held constant.

Systematic studies were made of the strengths of mortars in which the sand was replaced with salt (Table 12). In 28-day-cured specimens, the strength decreased from 42.6 MPa to 21.7 MPa as the salt concentration increased from 0 wt % to 63.2 wt %. The compressive strength was increased by the addition of fly ash (Fig. 15). The addition of 30 wt % fly ash to a saltcrete containing 30 wt % salt increased the strength from 24.2 MPa to >50 MPa. Contrary to the effect noted in neat cement pastes, there was essentially no difference between Kingston fly ash and Pueblo fly ash. In each case, the compressive strength varied approximately as follows:

Fig. 13. Compressive strengths of neat pastes as a function of curing time.

Fig. 14. Compressive strengths of neat pastes as a function of fly-ash content.

Fig. 15. Compressive strength of saltcrete as a function of fly-ash content. All samples contained 23 wt % type I Portland cement, 30 wt % salt, and 13.8 wt % water.

$$Y = 24.98 + 0.925X,$$

where Y is the compressive strength in MPa and X is the wt % fly ash.

Studies are currently under way to study the effect of class C and class H cements on the strengths of various possible candidates for bore-hole plugs. The initial specimens were neat cement pastes with a w/c of 0.60. After 28 days the compressive strengths were 15.5, 26.0, and 34 MPa for pastes made with class H, class C, and Type I respectively. These studies will continue in preparation for field tests to be made in the latter part of 1979.¹⁰

Table 12. Compressive strengths of saltcrete

Cement Type 1	Composition (wt %)			Compressive strength (MPa) after:	
	Salt	Sand	Water	28 days	91 days
23	0	63.2	13.8	32.6	45.5
23	10	53.2	13.8	24.2	29.1
23	30	33.2	13.8	24.7	26.2
23	63.2	0	13.8	21.7	19.0

2.3.3 Thermal conductivity

The thermal conductivities of the cement pastes, concretes, and saltcretes produced in this program are determined routinely. These data will be of value for determining temperature distributions and thermally induced stresses in cementitious structures and mine shaft seals located in the vicinity of high-level waste emplacements. The studies may eventually produce an effective model for calculating the thermal conductivities of concretes based on the composition and other physical properties. Results obtained thus far show that the thermal conductivity of the cementitious solids increases with density and with increased concentrations of sand and/or salt. Measurements made over a temperature range of 30 to 300°C show that the thermal conductivity of saltcrete decreases with increasing temperature but remains almost constant in neat cement pastes. The

thermal conductivity at 100°C ranged from 0.4 W/m·K for a neat cement paste to 1.8 W/m·K for a saltcrete.

A Dynatech TCFCM-20 comparative thermal conductivity analyzer was used to measure the thermal conductivities of the cementitious solids. In this instrument a short right-circular cylinder 2 in. OD x 0.5-1.0 in. high is sandwiched between two Pyrex 7740 reference discs of the same diameter (Fig. 16). Heat flows from the main heater at the top of the stack to the heat sink at the bottom. A second heater is used to control the temperature at the bottom. Metal spacers are placed between the heaters and the reference disks to equalize the heat flux over the horizontal cross section of the stack. A guard ring surrounding the stack was maintained at the same temperature gradient as that existing in the stack to prevent radial heat loss.

The temperatures are measured either by thermocouples embedded in grooves in the interface surfaces of the samples and reference materials or by temperature-sensing discs,¹² which are thin, circular plates of nickel into which a radial hole has been drilled for insertion of a thermocouple. Although the former technique is more accurate, the attendant sample preparation is quite time-consuming; thus the temperature-sensing discs are used for most screening measurements. After the required temperatures have been measured, the thermal conductivities are calculated from the equation

$$k_s = \frac{X_s}{2\Delta T_s} \left[\frac{k_t \Delta T_t}{X_t} + \frac{k_b \Delta T_b}{X_b} \right],$$

where

k = thermal conductivity, W/m·K;

ΔT = temperature differential, K;

X = thickness, cm;

s, t, b = subscripts referring to the sample, top reference, and bottom reference materials in the test stack respectively.

Although this equation is applicable in cases where the interface areas are equal and there is no radial heat flow, experimental results show that variations in area of less than 12% would change the results by less than 3%.

ORNL DWG 79-242

Fig. 16. Stack arrangement on thermal conductivity analyzer.

The precision of the measurements was determined by comparing one reference material with another using embedded thermocouples and temperature-sensing discs. Multiple determinations checked within 5% using embedded thermocouples. The values obtained with the discs were within $\pm 7\%$ of those using embedded thermocouples in 20 measurements and within $\pm 16\%$ in 10 others. The thermal conductivity of the reference material is known within $\pm 10\%$.¹³ Most of the measurements on concrete reported here were made using the sensing discs and are believed to be accurate within $\pm 20\%$.

Specimens are cut to the desired size with a SiC abrasive circular saw. The surfaces are then ground with water-cooled diamond laps for concrete specimens and SiC paper plus dry, loose grit for the saltcretes. The surfaces are made parallel to within 0.005 in. and flat to within 0.0005 in. with final polishing using SiC grit or Lucite laps. Specimens were then usually dried at least 16 hr at 130°C prior to the thermal conductivity measurements.

The thermal conductivities at 100°C of neat cement pastes, cement with fly ash, mortars, and saltcretes are presented in Tables 13, 14, 15, and 16 respectively. The data are tabulated for each category in the order of increasing density. In general, the thermal conductivity increased with density as expected (Fig. 17).

The thermal conductivities of neat cement pastes and saltcretes are plotted as a function of temperature in Fig. 18. It is evident that the thermal conductivity of a saltcrete decreases as the temperature increases; however, the values for the neat cement pastes show little, if any, significant change.

Further studies on the combined effects of density, porosity, additives, and water content may eventually produce an effective model for calculating the thermal conductivities of cementitious solids. Tokuda and Shoya¹⁴ investigated the effect of aggregate composition on the thermal diffusivity of saturated concrete but did not study saltcrete or address the effects of porosity and moisture content. Models for the calculation of thermal conductivity in porous materials have been developed by several investigators;^{12,15,16} however, none of these are as yet universally applicable.

Table 13. Thermal conductivities of neat cement pastes at 100°C

Type	Cement Number ^a	Composition (wt %)		Curing time (days)	Density (g/cm ³)	Thermal conductivity (W/m·K)
		Cement	Water			
M ^b	C-22	67.4	32.6	28	1.00	0.40
C	C-32	62.5	37.5	28	1.27	0.48
I	C-25	67.4	32.6	28	1.48	0.61
PC	C-21	67.4	32.6	28	1.50	0.62
CS II ^c	C-24	67.4	32.6	7	1.52	0.61
III	C-16	67.4	32.6	28	1.53	0.68
I	C-15	67.4	32.6	7	1.56	0.70
CS II ^c	C-24	67.4	32.6	7	1.57	0.63
I	C-15	67.4	32.6	7	1.58	0.72
I	C-15	67.4	32.6	28	1.58	0.73
I	C-20	67.4	32.6	91	1.59	0.70
I	C-15	67.4	32.6	28	1.62	0.72

^aSee Table 1.^bMortar mix supplied by the Giant Cement Co.^cChem Stress II.

Table 14. Thermal conductivities of cement--fly-ash pastes at 100°C

Cement: Type I Portland Number ^a	Fly ash Number ^a	Composition (wt %)			Curing time (days)	Density (g/cm ³)	Thermal conductivity (W/m·K)
		Cement	Fly ash	Water			
C-27	P-5	40.4	26.9	32.7	28	1.39	0.48
C-25	P-1	53.9	13.4	32.7	28	1.42	0.53
C-27	P-5	40.4	26.9	32.7	91	1.43	0.51
C-27	P-5	40.4	26.9	32.7	28	1.43	0.52
C-27	P-5	47.1	20.2	32.7	91	1.47	0.55
C-25	P-1	60.6	6.7	32.7	28	1.48	0.59
C-27	P-5	47.1	20.2	32.7	28	1.49	0.60
C-27	P-5	53.9	13.4	32.7	28	1.49	0.56
C-27	P-5	60.6	6.7	32.7	91	1.50	0.61
C-26	P-5	53.9	13.4	32.7	91	1.50	0.59
C-27	P-5	60.6	6.7	32.7	91	1.51	0.61
C-27	P-5	60.6	6.7	32.7	91	1.52	0.60
C-27	P-8	60.6	6.7	32.7	28	1.52	0.62
C-27	P-5	60.6	6.7	32.7	91	1.53	0.67
C-27	P-8	60.6	6.7	32.7	91	1.54	0.61
C-27	P-8	60.6	6.7	32.7	28	1.58	0.67

^aSee Table 1.

Table 15. Thermal conductivities of standard mortars at 100°C

Cement Type I Portland Number ^a	Composition (wt %)			Curing time (days)	Density (g/cm ³)	Thermal conductivity (W/m·K)
	Cement	Sand	Water			
C-27	40.4	26.9	32.7	91	1.51	0.81
C-27	53.8	13.5	32.7	91	1.52	0.73
C-27	47.1	20.2	32.7	91	1.55	0.74
C-26	40.4	26.9	32.7	28	1.56	0.76
C-27	53.8	13.5	32.7	91	1.56	0.78
C-26	53.8	13.5	32.7	28	1.57	0.65
C-26	47.1	20.2	32.7	28	1.60	0.79
C-12	67.3	0	32.7	28	1.60	0.80
C-27	53.8	13.5	32.7	91	1.60	0.76
C-26	40.4	26.9	32.7	91	1.60	0.87
C-28	23.0	63.2	13.8	28	1.95	1.76
C-28	23.0	63.2	13.8	91	1.97	1.20
C-28 °	23.0	63.2	13.8	28	2.00	1.71
C-28	23.0	63.2	13.8	28	2.01	1.72

^aSee Table 1.

Table 16. Thermal conductivities of saltcretes at 100°C

Cement Type I Portland Number ^a	Composition (wt %)					Curing time (days)	Density (g/cm ³)	Thermal conductivity (W/m·K)
	Cement	Sand	Salt	Fly ash	Water			
C-27	45.6 ^b	0	27.7	0	22.3	28	1.47	0.70
C-27	44.7	0	23.3	0	29.0	28	1.48	0.74 ^e
C-27	44.7	0	23.3	0	29.0	28	1.62	0.98
C-27	44.7	0	23.3	0	29.0	7	1.70	1.02
C-28	23.0	0	63.2	0	13.8	28	1.70	1.66
C-28	23.0	0	63.2	0	13.8	91	1.71	1.52
C-27	45.6 ^b	0	27.7	0	22.3	7	1.71	0.87
C-28	23.0	33.2	30.0	0	13.8	28	1.91	1.77
C-28	23.0	33.2	30.0	0	13.8	91	1.93	1.40
C-30	23.0	3.2	30.0	30.0 ^c	13.8	91	1.95	1.25
C-30	23.0	13.2	30.0	20.0 ^c	13.8	91	1.96	1.46
C-30	23.0	3.2	30.0	30.0 ^d	13.8	28	1.98	1.24
C-28	23.0	23.2	30.0	10.0 ^d	13.8	91	1.99	1.53
C-28	23.0	53.2	10.0	0	13.8	28	1.99	1.60
C-28	23.0	53.2	10.0	0	13.8	91	2.01	1.61
C-28	23.0	53.2	10.0	0	13.8	28	2.01	1.61

^aSee Table 1.^b4.4 wt % copper added.^cKingston (P-15) fly ash.^dPueblo (P-8) fly ash.^eAt 67°C.

Fig. 17. Thermal conductivities of cementitious solids at 100°C as a function of density.

Fig. 18. Thermal conductivities of a saltcrete and a cement paste as a function of temperature.

The solids in borehole plugs may eventually become immersed in a solution, possibly at high pressure, or at least in a humid atmosphere. Thus provisions should be made for determining thermal conductivities under such conditions. Preliminary thermal conductivity measurements made at 100°C on saturated saltcrete yielded values of 2.34 and 1.17 W/m·K for a saturated solid and a dry solid respectively. Saturation of the former sample may not have been complete since drying occurred as the measurements were being made. A cell for saturated samples, in which the sample is immersed in solution, was constructed based on experiments by Sass, Lachenbruch, and Monroe.¹⁷ This arrangement will be used in some of the future thermal conductivity measurements.

2.3.4 Permeability

The permeability of the plug solid to liquid flow is one of the major properties of interest. Current criteria require that the solids should have a permeability to water of 0.1 microdarcy after curing for 3 months.¹⁰ Measurements of liquid permeability are difficult and can be time-consuming; therefore, initial studies were primarily concerned with evaluating methods for measuring the permeabilities of solids to gases and converting the resulting values to those appropriate to fluid flow.¹⁸ Some preliminary studies, however, were started on liquid measurements.

Both liquid and gaseous permeability measurements are being made with a Hassler cell¹⁹ (see Fig. 19), which is widely used in the petroleum industry. In this system, a specimen is placed in a pliable sleeve such as neoprene, within a stainless steel jacket. After the sleeve has been sealed by applying hydraulic pressure to the outer sleeve surface, water or gas is forced through the ends of the specimen. The most critical steps in the procedure are the preparation and the drying of the specimen.

Preliminary results showed that the gas permeability of a cementitious solid could vary by three orders of magnitude, depending on the drying technique used with the specimen. The permeability values for specimens that contained 57 wt % Marquette Type I Portland cement, 10 wt % Kingston fly ash, and 33 wt % water and had been cured 28 days in saturated lime water ranged from 8×10^{-8} darcy after simple blot drying to 1.3×10^{-5} darcy after vacuum-drying for 24 hr. Other workers have shown that any

Fig. 19. Photograph of Hassler cell and system.

air-drying of a cementitious solid would result in loss of water of hydration with possible collapse of gel structure and microcracking.²⁰

After a number of drying methods had been examined, we selected a technique that produced specimens with minimum microcracking and yielded reasonably reproducible permeability data. As the first step of this technique, specimens are cut to the proper size (right-circular cylinders 2.5 cm in diameter by 2.5 cm long) and dried in a vacuum oven at 100°C and 50 μ pressure. Then they are allowed to dry until there is $\leq 0.1\%$ change in weight in 24 hr. An example of the permeability measurements obtained with duplicate specimens of saltcrete is shown in Fig. 20. Two specimens of a saltcrete containing 23.0 wt % Type I Portland cement, 20.0 wt % Kingston fly ash, 30 wt % salt, 3.2 wt % sand, and 13.8 wt % water were dried to constant weight. Subsequently, their permeabilities were measured using nitrogen gas. The equivalent fluid permeabilities were 1.15×10^{-5} and 1.00×10^{-5} darcy, respectively, a reasonable reproducibility for this type of measurement.

In the course of the drying studies, it was observed that microfractures that were not visually apparent were easily detected during gas permeability measurements. In applying the Klinkenberg correction to gas permeability data, specimens having microfractures showed an increase, rather than a decrease, in permeability at the higher pressures (Fig. 21). Since such an effect would not be observed in a liquid measurement, this technique will be used in the future to ensure that a specimen is crack-free prior to making a liquid permeability determination.

By using the vacuum drying technique and applying the Klinkenberg correction to determine the apparent liquid permeability, gas permeability measurements were made of a number of mortars having different sand concentrations as well as saltcretes with and without fly ash present (Table 17). Sand concentration appeared to have little effect on the apparent fluid permeability of the mortars; however, the permeabilities of the saltcretes decreased with increasing salt content, ranging from 6×10^{-7} darcy for 0 wt % salt to 1.25×10^{-8} darcy for 63.2 wt % salt. The addition of fly ash resulted in an increase in permeability. One would expect that, since the addition of fly ash leads to an increase in compressive

Fig. 20. Comparison of permeabilities of duplicate saltcrete samples dried to constant weight.

ORNL DWG 79-228R

Fig. 21. Permeability vs reciprocal pressure of a sample with microcracks.

strength, the resulting solids would exhibit lower permeabilities. Additional studies will be made to verify and explain these data.

Table 17. Permeabilities of mortars and saltcretes

Cement ^a	Composition (wt %)				Permeability (darcy)	
	Sand	Fly ash ^b	Salt	Water	28 days ^c	91 days ^c
60.6	6.7	0.0	0.0	32.6	5.6×10^{-5}	4.2×10^{-5}
53.9	13.5			32.6	9.7×10^{-5}	1.9×10^{-4}
47.2	20.2			32.6	6.0×10^{-5}	1.0×10^{-4}
40.5	26.9			32.6	1.2×10^{-5}	5.5×10^{-5}
23.0	63.2			13.8	6.6×10^{-7}	
23.0	53.2		10.0	13.8	2.2×10^{-7}	
23.0	33.2		30.0	13.8	4.8×10^{-8}	
23.0	23.2	10.0	30.0	13.8		1.2×10^{-6}
23.0	13.2	20.0	30.0	13.8		6.8×10^{-6}
23.0	3.2	30.0	30.0	13.8		1.0×10^{-5}

^aType I Portland cement.

^bP-15, Class F fly ash.

^cCuring time.

Liquid permeability measurements are in progress using a Hassler cell with an 80-psi pressure differential across the specimens. Tests with distilled water and mortars showed permeabilities about two orders of magnitude less than those obtained in gas measurements. For example, the apparent fluid permeability as determined by gas measurements for a mortar containing 47 wt % Type I Portland cement, 20 wt % sand, and 33 wt % water was 6.2×10^{-5} darcy. Water measurements made on the same specimen indicated a permeability of 7.8×10^{-7} darcy. A complete investigation is in progress to determine the precision and accuracy of these water permeability measurements.

2.3.5 Shrinkage characteristics

Bars of a number of different mixtures were cast, using ASTM procedure C490,⁹ to obtain information on the effect of composition on volume changes occurring in the resulting solids with time. After being allowed to cure for 24 hr at 30°C and >90% relative humidity, they were removed from the molds and hermetically sealed by wrapping with two layers of Parafilm M (to prevent any change in water content). It was assumed that under field conditions a plug solid, at least during the first few months, would not exchange any water with the surrounding environment. Weekly comparator readings of the bars were made for at least 26 weeks and the percent change in length calculated.

The solids examined in these tests showed two modes of shrinkage, plastic and autogenous. Since shrinkage should not continue indefinitely, a plot of the cumulative shrinkage vs time should produce a curve that asymptotically approaches a maximum value with time (Fig. 22). Assuming that the shrinkage rate is proportional to the maximum shrinkage minus the shrinkage (S) at time t, then

$$\frac{dS}{dt} = k(S_{\max} - S);$$

and by integration,

$$S = S_{\max}(1 - e^{-kt})$$

or

$$\ln \frac{1}{S_{\max} - S} = kt.$$

A plot of $\ln \frac{1}{S_{\max} - S}$ would be linear with t, thus confirming the relationship described above (Fig. 23). Some data on the saltcretes showed a linear relation during the time period examined (Fig. 24).

Mixtures containing fly ash showed two distinct rates of shrinkage (Fig. 25). The process that occurs during the setting period is known as plastic shrinkage and is of the order of 1% of the absolute volume of the dry cement.²⁰ Since each of the samples went through a 24-hr set period prior to these tests, it is not apparent whether the initial high rate of shrinkage exhibited by these specimens is part of the plastic

Fig. 22. Shrinkage of a saltcrete as a function of time.

ORNL DWG 79-231 R

Fig. 23. Logarithm of the reciprocal residual of shrinkage capacity as a function of time.

Fig. 24. Shrinkage of a saltcrete as a function of time, showing linear behavior.

ORNL DWG 79-233 R

Fig. 25. Shrinkage of a saltcrete as a function of time, showing two distinct shrinkage rates.

shrinkage or indicative of another mechanism. Continued hydration in the presence of ample water usually leads to expansion; however, shrinkage occurs when no moisture movement is permitted. This shrinkage, which is known as autogenous shrinkage, may be one of the types shown by these mixtures.

The magnitude of shrinkage in concrete is reported to be about 0.004% at the age of 1 month and 0.01% after 5 years. Values for the mixtures examined in these studies, which ranged from 0.011 to 0.176% are much higher than expected. In addition, the data showed poor reproducibility in that the total shrinkage values for similar mixes varied by factors of 2 to 3 (Table 18). Studies are currently being planned to pinpoint the changes that must be made in the procedures to improve the reliability of the data and to assess the significance of the shrinkage results.

2.4 Data Acquisition and Analysis

The DASAVOR program²¹ for storage and analysis of data collected in the Borehole Plugging Program was revised and divided into the Cement Data Acquisition and Sorting (CEDAS) and the Cement Experiment Analysis and Plotting (CEAP) programs. As the amount of data increased, the card sorting procedure in DASAVOR became cumbersome and excessive core space was needed. The card routine was replaced by a data sorting program. To decrease core space, the program was shortened by replacing the three-dimensional arrays with two-dimensional arrays. The CEAP program uses the DISSPLA graphics package²² for the plotting routine. The revised programs utilize both the PDP10 and the IEM 360/91 computers at ORNL. The PDP10 is used to acquire and sort data, and to provide terminal access to the IBM 360/91 for the analysis and plotting routine. Both programs are currently being tested prior to routine use.

Table 18. Effect of composition on volume reduction during curing

Composition ^a (wt %)			Shrinkage				Total shrinkage (%) (x 10 ³)
			Initial rate		Final rate		
			%/week (x 10 ³)	Time period (weeks)	%/week (x 10 ³)	Time period (weeks)	
Sand	Salt	Fly ash					
33.2	30.0	0.0			0.66	26	17
					0.74	26	19
					1.3	29	38
					1.4	30	42
	63.2				0.52	28	15
					0.73	26	19
					1.6	26	43
23.2	30.0	10.0	5.3	6	2.6	6-23	76
			8.4	7	1.6	7-26	89
13.2	30.0	20.0	16.0	5	1.6	5-25	110
3.2	30.0	30.0	36	4	1.7	4-23	176
23.2	30.0	10.0	11	8	1.8	8-18	106
			13	8	1.8	8-18	122
13.2	30.0	20.0	16	7	0.0	7-16	112
3.2	30.0	30.0	18	5	0.90	5-10	94
62.5 wt % Type C cement, 37.5 wt % water					1.5	11	16
					1.4	12	17
62.5 wt % Type I cement, 37.5 wt % water					1.4	8	11

^aIncludes 23.0 wt % Type I Portland cement and 13.8 wt % water except where noted.

3. FUTURE STUDIES

Field tests will be initiated in the latter part of 1979 to study borehole placement techniques using formulations developed by Sandia Laboratories.¹⁰ Thus, in the coming year, laboratory studies will be made with these recipes to ensure that they are suitable, or at least have no apparent objectionable qualities, for field testing. In addition, the parametric studies of the saltcretes and the pozzolanic concretes will continue, and an effort will be made to improve some of the testing procedures (e.g., the shrinkage tests). The overall long-term objective of the program is to develop cementitious mixes that will form stable solids for use in plugging boreholes in various geological media at or near waste repository sites. During the immediate future, work will be started on the development of accelerated durability test methods. Such tests will be required to demonstrate the high probability of having plug integrities and lifetimes equivalent to those of the repository site. A fairly complete research plan was developed for this program in collaboration with the Pennsylvania State University and is reprinted in the Appendix.

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6. APPENDIX: RESEARCH PLAN FOR "CEMENT TECHNOLOGY FOR
BOREHOLE PLUGGING" SUPPORTED BY THE
OFFICE OF NUCLEAR WASTE ISOLATION

John G. Moore

OBJECTIVES

The short-term objective (FY 1979) is to obtain sufficient data with selected Sandia recipes to determine their suitability for use as initial plug material for borehole plugging tests at the WIPP site.

The long-term objective (FY 1979-FY 1985) is to develop cementitious mixes that will form stable solids for use in plugging boreholes in various geologic media at or near waste repository sites. Accelerated test methods will be developed and durability data obtained during the course of this study to demonstrate the high probability of having plug integrities and lifetimes equivalent to those of the repository site.

A research and development program is being conducted in collaboration with the Pennsylvania State University (PSU) to achieve these goals and objectives. This study plan describes primarily the tasks in progress or to be initiated at the Oak Ridge National Laboratory (ORNL); however, since the tasks performed at PSU are required to achieve the objectives of the total program, they will be described briefly at the points where they supplement or augment the ORNL studies. Bimonthly meetings will be held by the program leaders of PSU and ORNL to discuss current results. When the data or circumstances warrant changes in direction or objectives, suitable alterations will be made in the studies.

This plan is divided into two major tasks. The first deals with the near-term objective of determining and assessing the suitability of the Sandia formulations for the borehole plug test program at the WIPP

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site. The second task is concerned with the derivation of products with sufficient natural characteristics to ensure long-term durability.

*Task 1: Characterization of the Initial Mixes to Be Used
in Borehole Plug Field Tests at the WIPP Site*

These field tests will be initiated in the latter part of 1979 and will use recipes previously developed by Sandia. Prior to these field tests, laboratory studies must be made with the recipes (up to six different mixes) to ensure that the formulations are suitable, or at least have no apparent objectionable qualities. The laboratory studies will cover:

1. wet mix properties,
2. properties of the solidified plug, and
3. interaction between the plug and the environment.

Properties of the Wet Mix

Some or all of the following ingredients will be used to prepare the plug: cement, fly ash, natural pozzolans, admixtures for reducing the water demand or friction, sand, and salt. Samples of the ingredients used will be subjected to physical and chemical analyses. The two laboratories, PSU and ORNL, will exchange samples for some specimen preparation and analytical evaluation. Mixes will be made according to the Sandia recipes furnished by ONWI. ORNL will make adjustments in the formulations in cases where it can be demonstrated that they will improve some desirable quality of the resulting solid.

The rheology, set time, hydration temperature, and bleed rate will be examined for each wet mix to ensure that the properties are adequate for placement in the borehole. The responsibilities can be outlined as follows:

Rheology	- ORNL will determine the slump by the K-meter technique. Flow curves and Fann Viscosity Measurements will be made on selected mixes.
	PSU will perform a systematic study of the rheology of cementitious mixes to improve methods for measuring viscosity and pumpability.

- Set time - ORNL will use the Penetrometer method and PSU the
 vicat method.
- Hydration - PSU
- Bleed rate - ORNL

Properties of the Solidified Plug

The specimens prepared from the wet mix will be cured in water-im-permeable containers or jackets so that only the mix water will be present during curing. Specimens will be cured for periods of 28 days, 91 days, 1 year, and >1 year. Physical tests will be made on all the cured solids. Evaluation of the long-term specimens need not be completed prior to the field tests. These specimens will be used in obtaining data relative to understanding the long-term behavior and durability of plug solids.

The tests and measurements to be made on the various specimens are listed below, along with the laboratory responsible for the major effort in the field cited. To ensure adequate precision and quality control, confirmation tests will be made periodically by the other laboratory.

- Compressive strength - ORNL will use 2-in. cubes; PSU will spot-
 check with cubes and measure the micro-
 hardness.
- Young's modulus - PSU
- Density - ORNL
- Porosity - ORNL will determine porosity with density
 measurements, helium pycnometer, and
 mercury intrusion.
- Permeability - ORNL will make gas permeability measure-
 ments on all specimens, and water or brine
 permeability measurements (low pressure)
 on the more-impermeable specimens. PSU
 will confirm with periodic high-pressure
 liquid measurements.
- Thermal conductivity - ORNL will measure the conductivities of
 all specimens.
- Thermal expansion - PSU

Thermal characterization	- PSU
Chemical characterization	- PSU; studies will include microstructure, morphology, and x-ray diffraction.
Volume change	- ORNL will use the standard bar test to determine the change that occurs after the first 24 hr. PSU will study the early (i.e., <24 -hr) volume change.

Interaction Between the Plug and the Environment

Studies will be made with solidified plug material in contact with geologic media and liquids from the area in question in order to obtain an estimate of the behavior of the plug mix in the WIPP site environment. Samples of the geologic media will be furnished by Sandia. The liquids will be simulated by using analytical values furnished by Sandia or ONWI.

Miniature boreholes will be made in samples of the geologic media and plugged with the various candidate mixes. Specimens will be cured for 91 days and >1 year prior to testing. ORNL will furnish specimens to PSU for chemical characterization before and after exposure in some of the environmental studies. The following tests will be made:

Plug/wall-rock permeability	- ORNL will determine the permeabilities of the wall rock and the plug solid, as well as the combination. Both liquid and gas will be used. In the case of liquid, the solution pushed through the specimen will be analyzed.
Plug/wall-rock bonding	- A push or pull strength test will be made at ambient conditions as well as at elevated temperatures and pressures.
Plug/wall-rock chemical interaction	- PSU will examine the microstructure to determine whether any reaction has occurred between the plug solid and the wall rock.

Effect of natural liquids

- ORNL will determine the solubility of the 91-day-cured plug material in liquids common to the WIPP site (i.e., brines and groundwaters). The tests will be run with and without wall rock present at ambient conditions as well as at an appropriate elevated temperature and pressure. PSU will explore the galvanic cell potentials between the plug and wall rock in the presence of natural fluids.

*Task 2: Long-Term Studies to Develop Durable Long-Lived
Solids for Borehole Plugs (FY 1979-85)*

Preliminary studies in the waste storage program showed that the only method currently available for plugging boreholes was high-quality cementing.* Thus, an investigation was initiated to develop cementitious mixes that would result in solids having a high probability of a long-lived service. There are numerous examples of concrete structures 300 to 500 years old, as well as a number of Roman structures that have shown durability for thousands of years. More significantly, many of the hydrated silicates found in concretes occur in nature and have lifetimes measured in geologic time.

The objective of this task is to produce cementitious mixes which, at the end of their hydration process, will become thermodynamically stable solids suitable for plugging holes in various geologic media. The initial solid must have characteristics such that environmental forces will not permeate them and change the course of hydration. Once the stable solid has formed, it must be shown that reactions with the local

* National Waste Terminal Storage Program Progress Report for the Period April 1, 1975, to September 30, 1976, Y/OWI-8 (Nov. 30, 1976).

environment are such that many thousands of years are required for any detrimental effect to occur. Thus, an accelerated durability test method must be developed, along with suitable models for interpreting the data, so that intelligent estimates may be made of the expected life span of actual combinations of plug and wall rock.

Many of the measurements and studies used to evaluate the plug solids produced in the long-term studies are the same as those in Task 1. The particular emphasis at ORNL and PSU is also the same as in Task 1. As the work progresses, it may be necessary to change or redirect one or more of the subtasks. Currently five different subtasks are associated with Task 2:

1. fly ash and saltcretes,
2. admixtures,
3. preparation of thermodynamically stable solids,
4. development of an accelerated durability test method,
5. reactivity of plug solids with the environment.

Fly Ash and Saltcrete

The parametric studies on the effect of fly ash and salt in cementitious solids will continue at ORNL. Fly ash will be used in the mix to decrease the permeability and to increase the sulfate resistance of the plug material. Salt is frequently used in cement slurries to bond the set cement more firmly to salt sections and shales encountered in the geologic media. The data obtained in these studies will show the effects of these materials on plug solids and will serve as the basis for the formulation of mixes leading to durable solids suitable for the various media encountered in a geologic repository.

Admixtures

The fundamental studies on the action of water- and friction-reducing admixtures in cementitious mixtures will continue at PSU. The data from these studies may provide the clues necessary for the formation of dense, impermeable, and hence more durable solids.

Preparation of Thermodynamically Stable Solids

This task will focus on the characterization of "old" concretes and the preparation of solids with known thermodynamically stable properties, starting with pure materials at whatever temperature and pressure that may be required. The goal is to establish the sequence of chemical or microstructural events that take place in this mixture as it develops into a stable solid. Following this, tests will be made with commercial materials at temperatures $<70^{\circ}\text{C}$ to determine the proportions required to prepare solids that will follow the same sequence of events. At the lower temperatures, it may be possible to determine only the first few steps of the hydration sequence in any reasonable time frame; however, if the sequence is well established in both cases, it should be possible to infer that the commercial mixture will, in some finite time, result in the same stable solid. Physical and durability tests can then be made with the final product, as well as at selected intermediate stages, to determine the overall suitability of the mixture as borehole plug material. The specific studies in this subtask will be carried out as follows:

Characterization of "old" concretes

- ORNL will make a literature survey, and PSU will review the resulting references. ORNL will help obtain samples for a systematic characterization study by PSU.

Preparation of stable solids

- PSU will use pure materials and establish the sequence of events; ORNL will use commercial materials. Physical and durability testing of the resulting solids will be done at ORNL; characterization studies will be carried out at PSU.

Development of an Accelerated Durability Test Method

ORNL and PSU will engage in a cooperative effort to have an accelerated durability test method in operation by the end of 1980. Preliminary studies will be initiated at ORNL using one of the better commercial mixtures developed to date. Specimens will be prepared and cured for periods of 3 days to >1 year at ambient temperature as well as at 40, 65, and 85°C. The specimens will be tested and characterized by ORNL and PSU as described in Task 1. The data from these tests will provide guidance for further studies.

Reactivity of the Plug Solids with the Environment

Solids prepared in Subtasks 2.3 and 2.4 will be contacted with fluids simulating those found at the WIPP site. Tests will be performed at ORNL at temperatures and pressures up to 250°C and 2500 psi for several time periods. The resulting fluids will be analyzed at ORNL. After selected physical tests have been made on the solids at ORNL, they will be shipped to PSU for chemical characterization.