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**Cement Technology for
Borehole Plugging: Interim
Report on the Effects of Fly
Ash and Salt on the Physical
Properties of Cementitious Solids**

J. G. Moore
M. T. Morgan
E. W. McDaniel
H. B. Greene
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CHEMICAL TECHNOLOGY DIVISION

NUCLEAR FUEL AND WASTE PROGRAMS

Cement Technology for Borehole Plugging

(Activity No. AG 30 10 03; 189 No. ONW-02802)

CEMENT TECHNOLOGY FOR BOREHOLE PLUGGING: INTERIM REPORT

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CONTENTS

ABSTRACT.....	1
1. INTRODUCTION.....	2
2. EXPERIMENTAL PROCEDURES AND MATERIALS.....	3
3. RESULTS AND DISCUSSION.....	4
3.1 Properties of the Wet Mix.....	4
3.2 Properties of the Cured Solids.....	7
3.2.1 Density and porosity.....	8
3.2.2 Compressive strength.....	11
3.2.3 Thermal conductivity.....	19
3.2.4 Permeability.....	22
3.2.5 Shrinkage characteristics.....	24
4. REFERENCES.....	24

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ABSTRACT

Results of initial studies of a systematic investigation to determine the effects of fly ash and salt on the physical properties of pozzolanic concretes and saltcretes are reported. The objective of this program is to develop cementitious mixes that will form thermodynamically stable solids suitable for plugging boreholes in various geologic media. In this first phase of the investigation, some of the problems and major effects in such cementitious systems have been identified and laboratory techniques have been developed.

The addition of fly ash to mortars decreased the set time and bleed characteristics and increased the compressive strength and permeability, but it had very little effect on the density or the thermal conductivity of the solid. The magnitude of these effects was only slightly related to the lime content of the fly ash.

In the case of saltcretes, the addition of a low-lime fly ash slightly decreased the set time and the bleed characteristics of the wet mix. However, a high-lime fly ash doubled the set time and decreased the bleed characteristics to essentially zero. The compressive strength of saltcretes was increased by the addition of fly ash and was independent of the lime content. Such additions had little effect on the thermal conductivity or density.

The thermal conductivities of cement pastes containing fly ash showed a near-linear relationship with the density of the resulting solids. In the case of mortars, the thermal conductivity decreased with increasing temperature and showed some hysteresis in the initial heating cycle. After the first cycle, the thermal conductivity decreased from about 1.32 W/m·K at 350 K to 1.27 W/m·K at 475 K.

These interim results have shown the need for more detailed studies on the effect of water and fly ash composition in these formulations and the necessity for developing a more accurate means of measuring time-dependent volume changes that occur in cementitious specimens.

1. INTRODUCTION

Isolation in geologic repositories located deep within the earth's crust is one of the more promising concepts for the storage and disposal of long-lived radioactive waste. All potential pathways in the vicinity of such a repository must be sealed to ensure the complete separation of the nuclides from man's environment. These pathways range from exploratory drill holes to mine shafts. The seals or plugs for these holes must maintain their integrity for thousands of years or more. Evaluations of existing methods and materials indicated that the most likely method currently available is high-quality cementing.¹ Investigations were thus initiated to improve current cementing technology to meet the more rigorous requirements for plugging boreholes near a radioactive waste terminal storage facility.

The long-term objective of the borehole plugging program in progress at the Oak Ridge National Laboratory (ORNL) is to develop cementitious mixes that will form thermodynamically stable solids suitable for plugging boreholes in various geologic media. A systematic study of the effects of fly ash and salt concentrations on the physical properties of pozzolanic concretes and saltcretes was undertaken as the initial phase of this generic investigation. The extreme age (>2000 years) of the many structures built with pozzolanic cements attests to the excellent durability of this type of concrete.² Fly ash, a readily available by-product of coal-burning electric power stations, serves as an excellent pozzolan and, in fact, offers some advantages over natural pozzolans.³ The physical properties of Portland cement-fly ash concretes are generally superior to ordinary Portland cement concretes,⁴ and the fly ash-cement mixtures offer a much higher resistance to chemical attacks.⁵ Because most of the previous studies have been concerned primarily with low-lime fly ashes, more research was needed for the high-lime ashes that are currently available.⁶ Thus systematic studies were initiated to determine the effect of lime in fly ash-cement solids, the influence of salt in such mixtures, and the eventual development of formulations that will lead to thermodynamically stable solids that meet the exacting requirements of borehole plugs.

Cement mixtures containing salt have been used for some time in the oil well industry to ensure good bonding between cement grouts and sections of salt or shale encountered in the wall rock surrounding a hole. The salt prevents the solubilization of the wall in a salt-containing geologic media and prevents the sloughing off or softening of walls containing clays or shales.⁷⁻¹⁰ Initial investigation of borehole plug formulations for the waste isolation pilot plant site indicated that salt may be required for certain sections of the plug and further study was recommended.^{11,12} Thus the parametric studies initiated at ORNL included saltcrete mixtures that might be appropriate for sealing boreholes in a variety of geologic media.

Data that examine the properties of cementitious mixtures containing salt and/or various fly ashes are presented. Studies made with neat cement pastes containing various concentrations of fly ash are described, and the results are given for a series of mortars in which various proportions of the sand in the standard mortar were replaced by either salt and/or fly ash. Although some permeability data will be presented in the discussions of the physical properties of all the solids under investigation, a separate detailed publication on permeability is being prepared because of the importance of this characteristic.¹³ Specimens have also been prepared for future geochemical and accelerated testing studies. Completion of these experiments will show if accelerated tests via elevated-temperature curing will simulate extended normal conditions.

2. EXPERIMENTAL PROCEDURES AND MATERIALS

Some or all of the following ingredients will probably be used to prepare borehole plugs: cement, fly ash and/or natural pozzolans, admixtures for reducing the water demand, sand, and salt. A systematic study of the effects that the concentrations of the various constituents have on the properties of the resulting solids is complicated by the complex interactions of the components. The standard mortar used as a control consisted of 23 wt % cement, 13.8 wt % water and 63.2 wt % sand. To obtain some measure of the effects of fly ash and salt, portions of the sand were replaced by salt and/or fly ash, but the cement and water

concentrations were unchanged; thus the water/cement (W/C) and water/solid (W/S) ratios remain constant throughout the set of experiments. In another series, cement was replaced by sand to vary the W/C ratio. In mixes containing pozzolans, the pozzolan was added to the dry cement and this mixture was treated as the cement phase in the ASTM standard mixing procedure.¹⁴ For saltcretes, the water was presaturated with salt and any remaining salt was treated as if it were sand in the standard mixing procedure.¹⁴ After allowing the wet mixes to set and cure, any changes in the physical properties of the resulting solids were then related to the changes in the composition. Complete descriptions of the materials as well as the experimental procedures used to make the specimens and to measure the physical properties were described previously.¹⁵

3. RESULTS AND DISCUSSION

3.1 Properties of the Wet Mix

When fly ash was added to mortars, the initial set times and the bleed characteristics (the appearance of water at the surface of the mix after placement) of the resulting mixes decreased with increasing fly ash concentration; the effect was more pronounced with P-8 than with P-15 fly ash (Table 1). The major difference in the compositions of the two ashes is in the total content of calcium oxide. The P-8, a lignite ash, contains 24.8 wt % calcium oxides whereas P-15, a bituminous ash, contains only 1.32 wt % (Table 2). This difference may be responsible for the variation in the effects observed, because the presence of excessive free lime would lead to a faster set as well as less bleeding. As noted below, these two fly ashes also produced very different results with saltcretes.

The addition of 10 wt % salt to a standard mortar approximately doubles the initial and final set times, but further additions of salt have little effect on either property (Table 3). The effects of adding fly ash to these saltcretes are highly variable and depend more on the composition of the fly ash than on the concentration used. The addition of 10 to 30 wt % P-15 fly ash to a 20 wt % saltcrete decreased the set time and the bleed characteristics slightly. However, P-8 fly ash

Table 1. Set time and bleed characteristics of mortars containing fly ash

Composition ^a					Set time		Bleed characteristics	
Type	Cement	Fly ash		Sand (wt %)	Initial (h)	Final (h)	Rate	Capacity
	Wt %	Number	Wt %				$\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^2 \cdot \text{s}}$	$\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^3 \text{ concrete}}$
I	62.5		0	0	6.2	8.0	<i>b</i>	<i>b</i>
I	23.0		0	63.2	5.5	8.4	7.67×10^{-5}	1.98×10^{-2}
I	23.0	P-15	10.0	53.2	4.5	6.4	2.33×10^{-5}	1.00×10^{-2}
I	23.0	P-15	20.0	43.2	3.9	6.5	1.06×10^{-5}	4.02×10^{-3}
I	23.0	P-15	30.0	33.2	3.7	6.3	0.0	0.0
I	23.0	P-8	10.0	53.2	5.1	7.1	1.46×10^{-5}	2.50×10^{-3}
I	23.0	P-8	20.0	43.2	1.1	2.4	0.0	0.0
I	23.0	P-8	30.0	33.2	<i>c</i>	<i>c</i>		

^aThe W/C ratio was 0.60 for all mixes.

^bNot measured.

^cToo stiff to mix.

Table 2. Fly ash analytical data^a

Fly ash 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-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-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-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	29.4	32.5	4.36	0.76	0.901	0.88	0.93	2.67	11.8	2.28	0.44	0.293

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

Table 3. Set times and bleed characteristics of saltcretes

Composition ^a		Set time		Bleed characteristics	
Salt (wt %)	Sand (wt %)	Initial (h)	Final (h)	Rate $\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^2 \cdot \text{s}}$	Capacity $\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^3 \text{ concrete}}$
0	63.2	5.5	8.2	7.67×10^{-5}	1.98×10^{-2}
10	53.2	11.6	16.1	2.69×10^{-5}	3.00×10^{-2}
30	33.2	12.5	16.8	1.41×10^{-5}	1.28×10^{-2}
63.2	0	10.9	14.5	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 = 0.60).

increased the set times about 50% but reduced the bleed characteristics to a level where they could no longer be measured (Table 4). The set times and bleed characteristics are important properties of any prospective borehole plug formulation, because sufficient time must be allowed to pump the mix to the region requiring plugging. In addition, bleeding should be kept to a minimum. These results demonstrate the quality control that will be required on any fly ash material used in borehole plug mixes.

3.2 Properties of the Cured Solids

The density, porosity, compressive strength, thermal conductivity, permeability, and shrinkage were determined for the various solids after curing them for a specified time at ambient temperature and pressure. The variables studied were the effect of curing time, cementitious mix composition, and fly ash composition. The experiments that have been completed and are being reported should be considered of a screening nature, although experimental techniques were developed, problems were identified, and major effects were distinguished. The next series should consist of detailed studies involving a more statistical approach at temperatures, pressures, and in the presence of geological media likely to be encountered in actual plugging situations.

Table 4. Set time and bleed characteristics
of saltcretes containing fly ash

Composition ^a			Set time		Bleed characteristics	
Fly ash		Sand (wt %)	Initial (h)	Final (h)	Rate $\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^2 \cdot \text{s}}$	Capacity $\frac{\text{cm}^3 \text{ H}_2\text{O}}{\text{cm}^3 \text{ concrete}}$
No.	Wt %					
P-15 ^b	0	33.2	12.5	16.8	1.41×10^{-5}	2.28×10^{-2}
	10	23.2	8.7	11.7	1.71×10^{-5}	1.02×10^{-2}
	20	13.2	10.5	13.9	9.80×10^{-6}	1.44×10^{-2}
	30	3.2	9.7	13.8	2.6×10^{-6}	4.1×10^{-3}
P-8 ^c	10	23.2	15.4	19.4	9.43×10^{-6}	6.74×10^{-3}
	20	13.2	20.0	25.6	2.05×10^{-6}	9.80×10^{-3}
	30	3.2	19.6	24.6	$<7.0 \times 10^{-7}$	$<1.0 \times 10^{-4}$

^aAll mixes contained 23.0 wt % Marquette Type I Portland cement, 13.8 wt % H₂O (W/C ratio = 0.60), and 30 wt % NaCl.

^bP-15 fly ash contains 1.32 wt % total CaO (see Table 2).

^cP-8 fly ash contains 24.78 wt % total CaO (see Table 2).

3.2.1 Density and porosity

Density and porosity are important properties in the study of cementitious materials because they have a strong influence on the permeability and the thermal conductivity of solids. Since moisture content affects the density values determined for porous materials, extensive saturation and drying studies were conducted to establish an optimum procedure. The procedure selected consisted of vacuum drying at 100°C for at least 48 h and until the daily weight change was less than 0.1%. The porosity values were obtained by subtracting the dry density from the saturation density. This saturation of the solid was accomplished by immersion in the appropriate liquid until the daily weight change was less than 0.1%.¹⁵

Previous data showed that, in general, porosity decreased with increasing density.¹⁵ Additional densities have been measured and are shown in Tables 5 to 7. The addition of fly ash or salt to the mortars produced only slight changes in the densities of the resulting solids. Additional data are required to distinguish between the effects of the composition of the solids and the water-to-solids ratio.

Table 5. Density of cement pastes

Cement		Fly ash		Water (wt %)	Density	
Type	Wt %	Type	Wt %		28 days	91 days
I	62.5		0	37.5	1.356	1.452
C	62.5		0	37.5	1.292	1.324
H	62.5		0	37.5	1.567	1.565
I	67.3		0	32.7	1.602	1.589
C	67.3		0	32.7	1.529	
I	60.6	P1	6.7	32.7	1.450	
I	60.6	P2	6.7	32.7	1.450	
I	60.6	P5	6.7	32.7	1.537	1.531
I	60.6	B8	6.7	32.7	1.557	1.550
I	53.8	P1	13.5	32.7	1.425	
I	53.8	P5	13.5	32.7	1.491	1.485
I	47.1	P5	20.2	32.7	1.471	1.457
I	40.4	P1	26.9	32.7	1.378	
I	40.4	P5	26.9	32.7	1.433	1.407

Table 6. Density of mortars

Cement		Sand (wt %)	Fly ash		Water (wt %)	Density	
Type	Wt %		Type	Wt %		28 days	91 days
I	67.3	0		0	32.7	1.602	1.589
I	60.6	6.7		0	32.7	1.560	
I	53.8	13.5		0	32.7	1.596	1.549
I	47.1	20.2		0	32.7	1.581	1.540
I	40.4	26.9		0	32.7	1.563	1.560
I	23.0	63.2		0	13.8	2.019	1.982
C	23.0	63.2		0	13.8	1.943	1.945
H	23.0	63.2		0	13.8		1.920
I	23.0	53.2	P15	10	13.8	2.056	2.023
I	23.0	53.2	P8	10	13.8		2.067
C	23.0	53.2	P15	10	13.8		1.991
C	23.0	53.2	P8	10	13.8		2.045
H	23.0	53.2	P15	10	13.8		2.038
H	23.0	53.2	P8	10	13.8		2.058
I	23.0	43.2	P15	20	13.8		1.964
I	23.0	43.2	P16	20	13.8		1.979
I	23.0	43.2	P8	20	13.8	2.009	2.078
I	23.0	43.2	P17	20	13.8		2.042
C	23.0	43.2	P15	20	13.8		1.942
C	23.0	43.2	P16	20	13.8		1.966
C	23.0	43.2	P8	20	13.8		2.004
C	23.0	43.2	P17	20	13.8		2.035
H	23.0	43.2	P15	20	13.8		1.971
H	23.0	43.2	P16	20	13.8		1.984
H	23.0	43.2	P8	20	13.8		2.054
H	23.0	43.2	P17	20	13.8		2.089
I	23.0	33.2	P15	30	13.8		1.895
H	23.0	33.2	P15	30	13.8		1.924

Table 7. Density of saltcretes^a

Sand (wt %)	Salt (wt %)	Fly ash		Density	
		Type	wt %	28 days	91 days
63.2	0		0	2.019	1.982
53.2	10		0	2.014	1.985
33.2	30		0	1.914	1.917
23.2	30	P15	10		1.971
23.2	30	P8	10		1.926
13.2	30	P15	20		1.966
13.2	30	P8	20		1.909
3.2	30	P15	30	1.980	
3.2	30	P8	30		1.951
0	63.2		0	1.676	1.660

^aAll mixes contained 23 wt % Type I Portland cement and 13.8 wt % water.

3.2.2 Compressive strength

Compressive strength measurements were made by crushing standard 2-cm cubes that had been prepared according to ASTM procedure C-109¹⁴ and placed in a humidity cabinet (>90% relative humidity and 28°C) to solidify. After 24 h, 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.

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 of 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.

Compressive strength measurements were made on mortars containing various concentrations of sand, neat cement pastes containing different fly ashes, and saltcretes with and without the presence of fly ash. The values determined for the mortars served as reference points for the fly ash and saltcrete parametric studies. The mortars, which had a water-to-cement plus 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 (Fig. 1). The compressive strength varied as follows:

$$\begin{aligned} \text{7-day curing} \quad Y &= 24.7 - 0.48 X, \\ \text{28-day curing} \quad Y &= 39.8 - 0.794 X, \\ \text{91-day curing} \quad Y &= 45.3 - 0.47 X, \end{aligned}$$

where Y is the compressive strength in MPa and X is the weight percent of sand present in the mortar.

An approximately linear relationship was found to exist between the compressive strength of concrete and the cement/water (C/W) ratio over the range for C/W ratios of 1.2 to 2.5 (W/C ratio of 0.4 to 0.8). This relationship was expressed by Inge Lyse² as:

$$S = X + Y (C/W),$$

where S is the compressive strength and X and Y are empirical constants derived from the data in question. This is the apparent relationship for the data obtained from neat cement pastes cured 7 and 28 days (Figs. 2 and 3), and, with one exception, it is also true for the 91-day cured paste (Fig. 4). The major change in the relationship that was observed when fly ash was added to the paste is a decrease in the slope of the line. Much additional data are needed for different fly ash compositions and over a wide range of mix formulations before any basic relationships can be established between the concentration and composition of the fly ash and the compressive strengths of cement-fly ash mixtures.

The addition of fly ash to mortars increased the compressive strength of the resulting solids and reached a maximum at a fly ash concentration of about 20 wt %. The compressive strengths after short curing times

Fig. 1. Compressive strengths of mortars as a function of sand content.

ORNL DWG 79-1639

Fig. 2. Compressive strength of Type I Portland cement pastes with and without fly ash present after curing 7 days at ambient temperature.

ORNL DWG 79-20516

Fig. 3. Compressive strength of Type I Portland cement pastes with and without fly ash after curing 28 days at ambient temperature.

Fig. 4. Compressive strength of Type I Portland cement pastes with and without fly ash after curing 91 days at ambient temperature.

(28 days) were higher for solids containing fly ashes with a higher lime content, but this difference became less significant after longer periods (91 days). This would be expected because lime is known to contribute to early strength, whereas the pozzolanic reactions between fly ash and cement require more time. In all of these tests, the mortars contained 23 wt % cement, 13.8 wt % water and 63.2 wt % total sand plus fly ash. The total lime content of the fly ashes varied from 1.3 to 40.3 wt % (Table 8).

The substitution of salt for part of the sand in standard mortars produced solids (saltcretes) with lower compressive strengths (Fig. 5). The addition of fly ash to saltcretes containing 30 wt % salt increased the compressive strength proportional to the concentration of fly ash.

Table 8. Compressive strength of mortars with different types of cement and fly ash^a

Fly ash			Compressive strength of mortar vs types of cement (MPa)					
Concentration in mortar (wt %)	Type	CaO content (wt %)	Curing time, 28 days			Curing time, 91 days		
			Type I	Class C	Class H	Type I	Class C	Class H
0			42.7	37.2	22.8	45.1	41.1	32.1
10	P15	1.3	52.2	43.2	36.1	71.3	65.1	62.1
10	P8	24.8	46.3	67.2	56.2	61.2	65.4	59.9
20	P15	1.3	50.0	53.7	44.6	70.8	62.7	58.1
20	P16	7.4	58.0	61.0	51.5	75.2	76.9	64.2
20	P8	24.8	60.3	61.6	63.9	71.0	72.8	69.2
20	P17	40.3	74.4	66.6	62.4	75.9	76.9	78.2
30	P15	1.3	47.7	<i>b</i>	<i>c</i>	69.5	<i>b</i>	60.1

^a All specimens contained 23 wt % cement, 63.2 wt % sand plus fly ash, and 13.8 wt % water with a W/C ratio of 0.600.

^b Was too stiff to form specimens.

^c Not measured.

Fig. 5. Compressive strength of saltcretes as a function of salt concentration.

In this case, the composition of the fly ash had little, if any, effect. High- and low-lime fly ashes produced about the same increase in strength (Fig. 6 and Table 9). In all these tests, the solids were made to contain 23 wt % cement, 13.8 wt % water, and a total of 63.2 wt % sand plus salt plus fly ash.

Fig. 6. 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.

Table 9. Effect of fly ash composition and concentration on the compressive strength of saltcretes^a

Fly ash concentration (wt %)	Sand concentration (wt %)	Compressive strength of mortar (MPa)			
		Type P15 fly ash ^b		Type P8 fly ash ^b	
		28 days	91 days	28 days	91 days
0	33.2	24.7	26.2	24.7	26.2
10	23.2	33.4	51.8	34.1	46.4
20	13.2	45.6	58.3	45.0	52.0
30	3.2	51.2	57.2	52.2	57.5

^aAll mixes contained 23 wt % Type I Portland cement, 30 wt % salt, 33.2 wt % sand plus fly ash, and 13.8 wt % water.

^bSee Table 2.

3.2.3 Thermal conductivity

The thermal conductivities of the concretes and neat pastes were determined using a Dynatech TCFCM-N20 comparative thermal-conductivity instrument controlled by a Hewlett Packard Model 3052A data acquisition system. Temperature-sensing discs were used in place of embedded thermocouples in most of the measurements. The temperature-sensing discs are thin circular plates of nickel into which a radial hole was drilled for insertion of a thermocouple. This method eliminates the time-consuming installation of thermocouples in the samples and has a precision of better than $\pm 10\%$ as compared to $\pm 5\%$ for imbedded thermocouples. The more accurate method of embedded thermocouples was used for the thermal conductivity vs temperature study and for spot checks of measurements made with the discs. Details of this method have been described previously.^{15,16}

The thermal conductivities of cement pastes containing fly ash show a near-linear relation with density (Fig. 7). The thermal conductivities of mortars show some correlation with density at sand concentrations up to 43%; however, thermal conductivity increases while density decreases at higher concentrations (Fig. 8), because the thermal conductivity of the sand is significantly higher than that of cement. The same effect is observed with high concentrations of salt in saltcrete. The thermal conductivity of all of the cementitious solids is somewhat linear with density up to these limiting concentrations (Fig. 9). Further study is necessary to produce a more exact correlation between thermal conductivity and the variables in cementitious solids which affect it.

The thermal conductivity of mortars decrease with increasing temperature and show hysteresis on the initial heating cycle (Fig. 10). The hysteresis resulted in a lower thermal conductivity ($\sim 4\%$ at 373 K) after the initial heating cycle to ~ 550 K. However, no further reduction in thermal conductivity with continued cycling was observed. This effect

Fig. 7. Thermal conductivity of a Type I Portland cement paste containing fly ash.

Fig. 8. Thermal conductivity of mortars.

ORNL DWG 79-243R2

Fig. 9. Thermal conductivities of cementitious solids at 100°C as a function of density.

ORNL DWG 79-1641

Fig. 10. Thermal conductivity of a mortar vs temperature.

is similar to that observed in studies on rock and is attributed to irreversible structural change in the rocks and cement caused by the initial heating cycle.^{17,18}

The thermal conductivities are linear with temperature over the range measured and within the scatter of the data. Equations obtained by linear least-squares fit were:

$$k = 1.67 - 7.88 \times 10^{-4} T \text{ for the initial heat up cycle, and}$$

$$k = 1.473 - 4.343 \times 10^{-4} T \text{ for conductivities after reaching maximum temperature}$$

where

k = thermal conductivity (W/m·K) and

T = absolute temperature (K).

3.2.4 Permeability

The major objective of a borehole plug is to prevent the borehole from serving as a pathway for the movement of liquids to and/or from a radioactive waste repository. Thus the permeability of the plug solids and the plug-wall-rock junctions is a property of major concern. The results of the investigation of the permeability of various cementitious mixtures is reported elsewhere¹³ and only some of the data will be summarized here.

Briefly, in those tests, standard mortars containing 10 to 30 wt % fly ash had permeabilities of about 10^{-5} darcy and were somewhat dependent on the lime content of the fly ash. For example, a standard mortar in which 20 wt % of the sand was replaced by fly ash containing 1.3 wt % CaO had a permeability of 2.5×10^{-5} . Under the same conditions, a fly ash containing 40.3 wt % CaO resulted in a solid with a permeability of 6×10^{-5} darcy.

Further results showed that using salt to replace 10 to 30 wt % of the sand in a standard mortar produced saltcretes with permeabilities of 2×10^{-7} to 5×10^{-8} darcy. The substitution of fly ash for the remaining sand increased the permeability by almost three orders of magnitude and was dependent on the type and amount of fly ash.¹³

3.2.5 Shrinkage characteristics

Length-change measurements were made using a length comparator, as described in ASTM specification C490.¹⁴ The specimens were prisms cast in a nominal length of 25.4 cm. They were removed from the mold after 24 hr, sealed in an impervious film and measured periodically. Control specimens were cured in saturated lime water according to ASTM specifications.¹⁴ The sealed specimens probably represented more closely the conditions that would exist in a borehole plug. The shrinkage, S (%), is given by

$$S = 100 \frac{(R-P) - (R_o - P_o)}{10 - (R_o - P_o)}$$

where R and P are the comparator readings in inches of a reference bar and prism, respectively, and R_o and P_o are the initial readings.

Length changes were determined for periods as long as 420 days. In most cases, shrinkage ceased after 200 to 300 days and a slight reversal was noted in some samples. The maximum shrinkage ranged from 0.02% to 0.19% (Table 10). The highest shrinkage occurred in saltcretes in unsealed mortars. The presence of fly ash apparently had no effect. However, these measurements were very erratic, and a more accurate method of measuring length change must be developed before models and mechanisms can be examined.

Table 10. Length change of mortars and saltcretes

Cement type ^a	Sand (wt %)	Salt (wt %)	Fly ash		Storage condition ^b	Maximum shrinkage (% of length)
			Concentration (wt %)	No.		
I	63.2	0	0		U	0.11
	63.2	0	0		S	0.028
	33.2	30	0		S	0.12
	0	63.2	0		S	0.037
	33.2	30	0		S	0.12
	23.2	30	10	P15	S	0.085
	23.2	30	10	P8	S	0.11
	13.2	30	20	P15	S	0.11
	13.2	30	20	P8	S	0.28
	3.2	30	30	P8	S	0.13
	63.2		0		U	0.11
	63.2		0		S	0.028
H	53.2		10	P15	S	0.043
I	43.2		20	P15	S	0.023
	43.2		20	P16	S	0.029
	43.2		20	P8	S	0.018
	43.2		20	P17	S	0.036
C	43.2		20	P15	S	0.023
	43.2		20	P16	S	0.044
	43.2		20	P8	S	0.036
	43.2		20	P17	S	0.041
H	43.2		20	P15	S	0.037
	43.2		20	P16	S	0.025
	43.2	0	20	P8	S	0.026
	43.2	0	20	P17	S	0.038
	33.2	9	30	P15	S	0.031

^aAll mixes contained 23 wt % cement, 63.2 wt % sand + salt + fly ash, and 13.8 wt % water.

^bU = unsealed, S = sealed.

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