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Thermophysical Properties of Heat Resistant Shielding Material

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THERMOPHYSICAL PROPERTIES OF HEAT RESISTANT SHIELDING MATERIAL

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1. INTRODUCTION

This project was aimed at determining thermal conductivity, specific heat and thermal expansion of a heat resistant shielding material for neutron absorption applications. These data are critical in predicting the structural integrity of the shielding under thermal cycling and mechanical load. The measurements of thermal conductivity and specific heat were conducted in air at five different temperatures (-31ºF, 73.4ºF, 140ºF, 212ºF and 302ºF). The transient plane source (TPS) method was used in the tests. Thermal expansion tests were conducted using push rod dilatometry over the continuous range from -40°F (-40°C) to 302°F (150°C).

2. EXPERIMENTAL

2.1 THERMAL CONDUCTIVITY AND VOLUMETRIC SPECIFIC HEAT

The Hot Disk Thermal Constants Analyzer was used to measure both thermal conductivity and specific heat of the samples.[1-3] The recently upgraded system (Fig. 1) uses a bridge to balance out changes in heater resistance at different temperatures. Two samples are needed for the measurement. A Kapton sensor/heater is sandwiched between the two samples. For the heat resistant shielding material, each measurement took 80 s during which the interface was heated up by a constant power output of 0.05 W. The overall temperature rise was kept under 5ºC. Thermal conductivity and volumetric specific heat can be calculated from the interface temperature vs. time plot using the Hot Disk® software.

Six heat resistant shielding samples, Thermo Electron RM&P Catalog No. 277-4, were provided and were paired up in random. Each pair was measured at room temperature at HTML. The system was then taken to Building 4508 where a freezer (at -31ºF) was available. After the freezer test, the specimens were tested in a box furnace at three elevated temperatures. To reach thermal equilibrium, the specimens were left in the freezer or furnace for at least 2.5 hr before measurements were started.

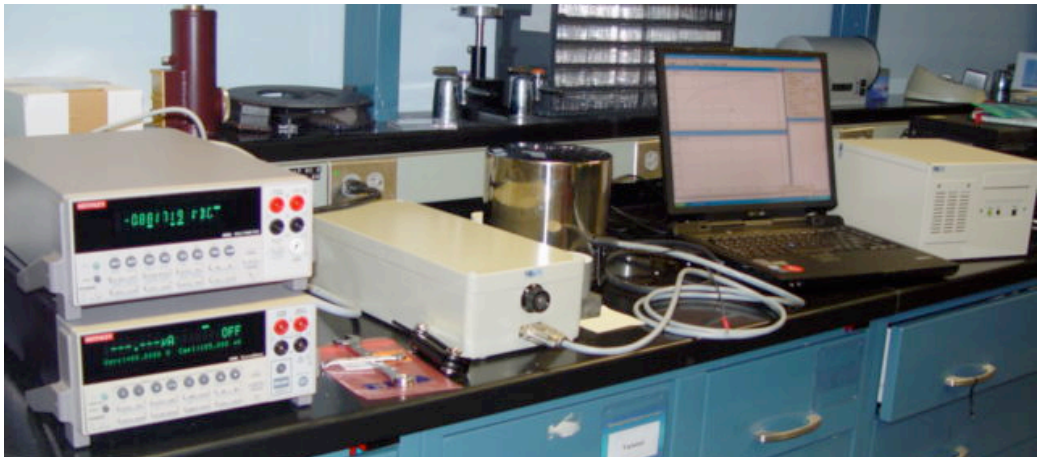

Fig. 1. Hot Disk System.

2.2 THERMAL EXPANSION

Specimens of cast Type 277-4 cement were received and tested by staff of the High Temperature Materials Laboratory at ORNL. The specimens were received in two shipments and consisted of three separate pours (lots) of the material. Lot 1 contained one specimen, poured in a one-piece mold, and having a diameter of ~5.5 mm. Lot 2 contained 7 specimens, poured in a split two-piece mold, also with a diameter of ~5.5 mm. Lot 3 had 5 specimens with a diameter of ~12.5 mm. No specimens from Lot 3 were used for measurements. The nominal length of all specimens was 25 mm.

Thermal expansion measurements were conducted using a Theta Industries dual push rod dilatometer. The testing followed the constant ramping procedure of ASTM E-228 for "Linear Thermal Expansion of Solid Materials with a Vitreous Silica Dilatometer."[4] A cryogenic furnace, cooled with helium gas bubbled through liquid nitrogen and heated by nichrome wires, was used with a silica specimen holder and push rods. A type K thermocouple in direct contact with the specimen was used to measure the specimen temperature. NIST Tungsten SRM 737 was used for the reference standard in the differential measurements. The specimens were tested over the range of -40°C to 150°C using heating rates of 3°C/min. The reference temperature for all expansion calculations was 20°C. A 5 cc/min flowrate of helium was used inside the specimen enclosure during the tests. This was a separate stream of helium from that used for cooling the cryogenic furnace. The displacements of the specimen and reference rods were determined by an LVDT housed in a constant temperature enclosure which also contained the RTD used for cold junction compensation of the specimen thermocouple signal.

The temperature schedule for the measurement tests was as follows:

1. Cool specimen to ~15°C prior to starting test using cooled helium.
2. Start data collection and heat specimen to 40°C. (Expansion is automatically zeroed as the specimen temperature goes through the 20°C reference temperature.)
3. Cool to -40°C at a nominal rate of 3°C/min.
4. Heat to 150°C.
5. Cool to -40°C at a nominal rate of 3°C/min.
6. Heat to 25°C and end test.

The schedule used allowed any hysteresis of the specimen expansion behavior to be noted.

3. RESULTS

3.1 THERMAL CONDUCTIVITY AND VOLUMETRIC SPECIFIC HEAT

Thermal conductivity values of the three pairs of samples are shown in Table 1 and the Thermal Conductivity vs. Temperature plot is shown in Fig. 2. Three measurements were taken at each temperature for each pair of samples. There is some scatter among the pairs (<5% between 3 measurements at the same temperature, 3-10% among the pairs) but they all showed similar changes over the temperature range. Since the specimens had to be taken out several times at each temperature, their exposure to air and thermal cycles was not controlled.

Table 1. Thermal conductivity (W/m•K)

Temperature (F)	Pair A	Pair B	Pair C
-31	0.96	0.97	0.92
73.4	1.00	0.97	1.05
140	0.87	0.75	0.87
212	0.64	0.62	0.58
302	0.67	0.59	0.64

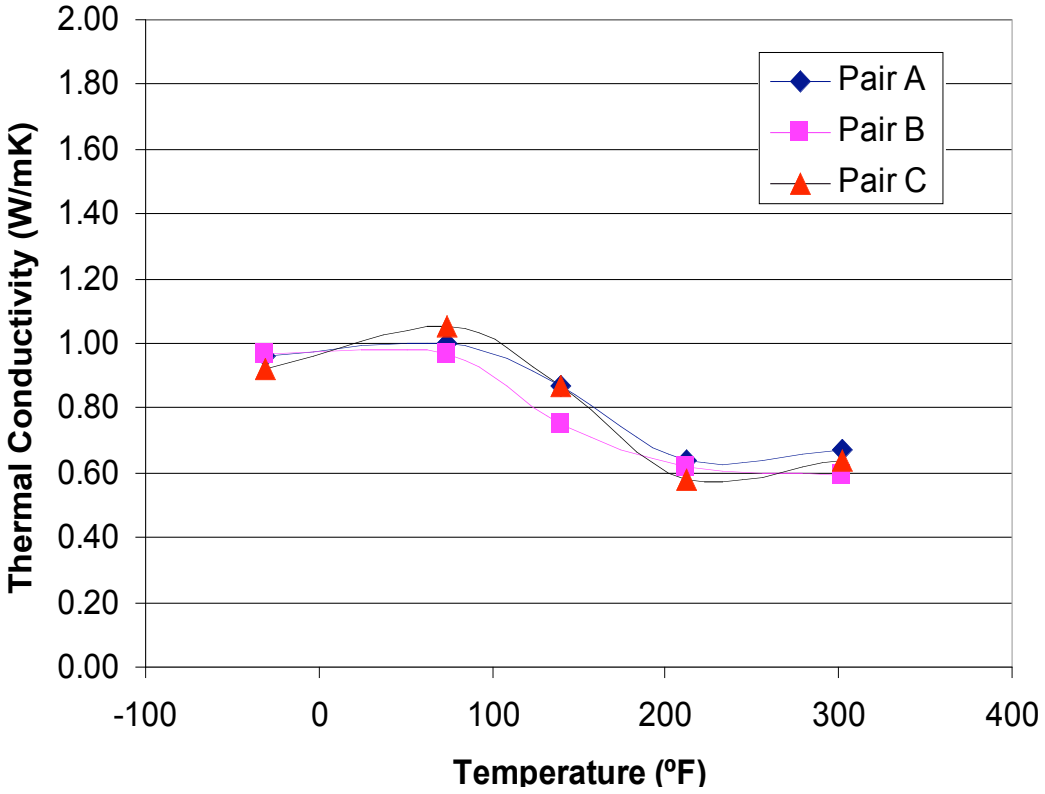

Fig 2. Thermal conductivity of Thermo Electron RM&P Catalog No. 277-4.

The volumetric specific heats were also obtained in the calculation. The value is a product of specific heat and density with the unit of $10^6 J/m^3 \cdot K$, as shown in Table 2 and Fig. 3. Since the weight of the samples exceeded the limit of the balance in the lab we were not able to measure the density of the specimens accurately. If the density is known ($1.68*10^6 g/m^3$ from product literature), the specific heat values can be calculated simply by dividing the current experimental value by density.

Table 2. Volumetric Specific Heat (MJ/m^3•K)

Temperature (F)	Pair A	Pair B	Pair C
-31	0.92	0.80	0.92
73.4	1.33	1.27	1.32
140	1.71	1.68	1.65
212	1.72	1.67	1.72
302	1.99	2.14	2.01

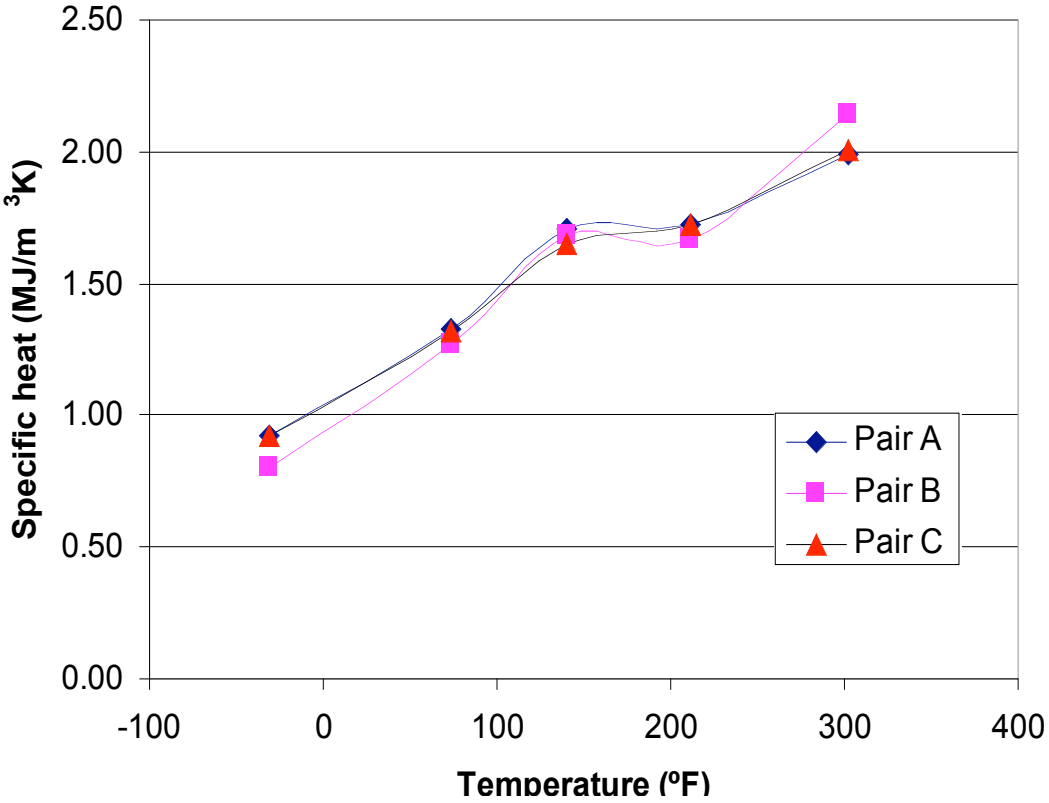

Fig. 3. Volumetric specific heat vs. temperature.

Since the three pairs of specimens were randomly grouped, we averaged the results to show the material properties. The values are shown in Table 3 and the plots are shown in Figures 4-5.

Table 3. Average values of k and Cp

Temperature (°F)	Average k (W/m•K)	Average Cp (MJ/m^3•K)
-31	0.95	0.88
73.4	1.01	1.31
140	0.83	1.68
212	0.61	1.70
302	0.63	2.05

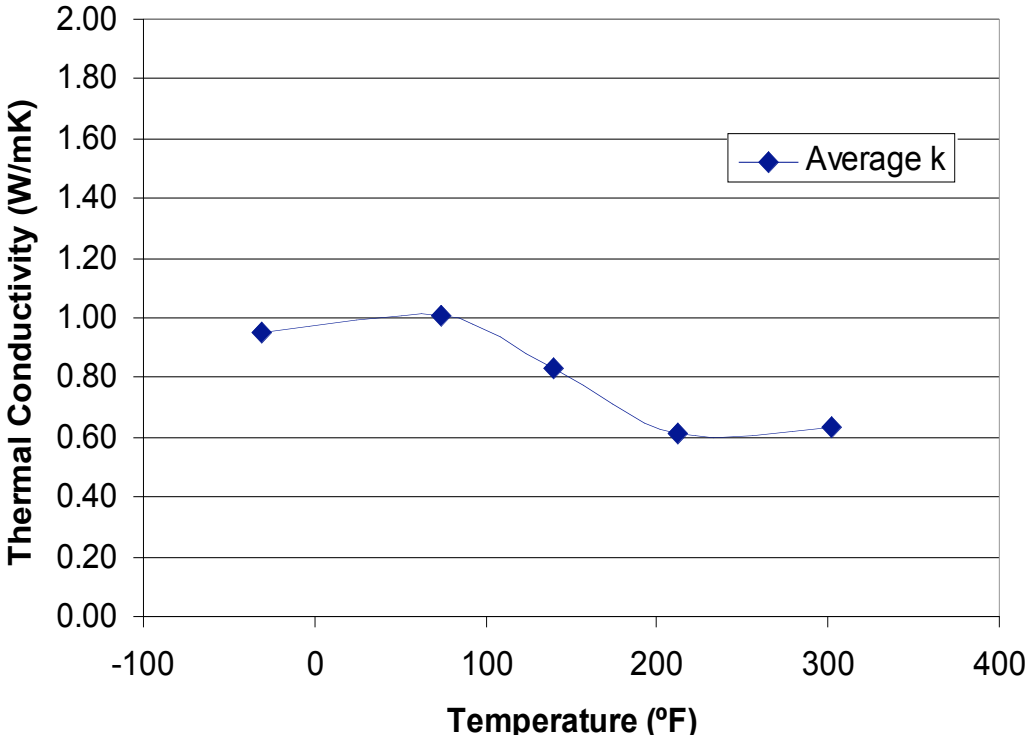

Fig. 4. Average thermal conductivity of Thermo Electron RM&P No. 277-4.

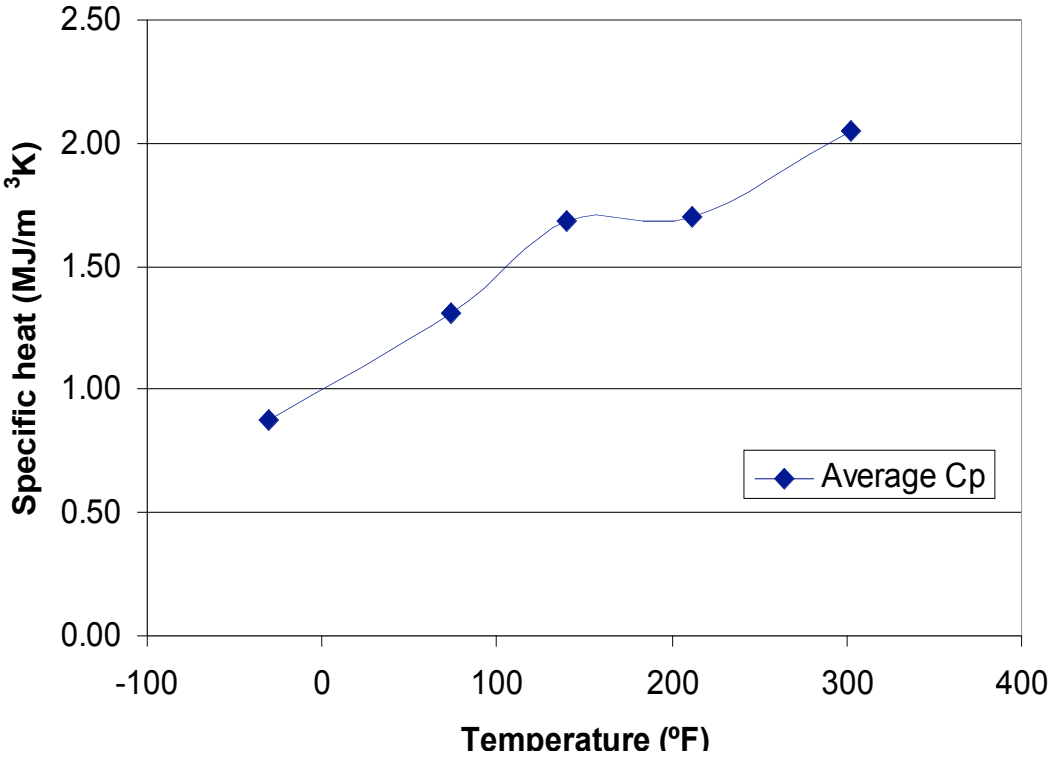

Fig. 5. Average volumetric specific heat of Thermo Electron RM&P Catalog No. 277-4.

3.2 THERMAL EXPANSION

One specimen from Lot 1 and four specimens from Lot 2 were tested. The thermal expansion results of the five specimens are shown in Fig. 6. Three Lot 2 specimen results grouped almost on top of each other. The fourth Lot 2 specimen deviated from the other three at temperatures greater than about 100°C. The single specimen from Lot 1 behaved markedly different than the Lot 2 specimens when heated above 50°C. The expansion behavior during cooling was very similar for all five specimens tested. All specimens tested exhibited a permanent strain (shrinkage) as a result of heating above 50°C. Measured data for the expansion of the five specimens taken from the initial heating from -40°C to 150°C can be found in Table 4. Also shown in Table 4 are values for the Mean Coefficient of Thermal Expansion (MCTE) calculated from 20°C. MCTE is defined as:

$$\text{MCTE} = (\text{expansion @ T}) / (\text{T} - 20) \quad (1)$$

where T is the temperature in °C.

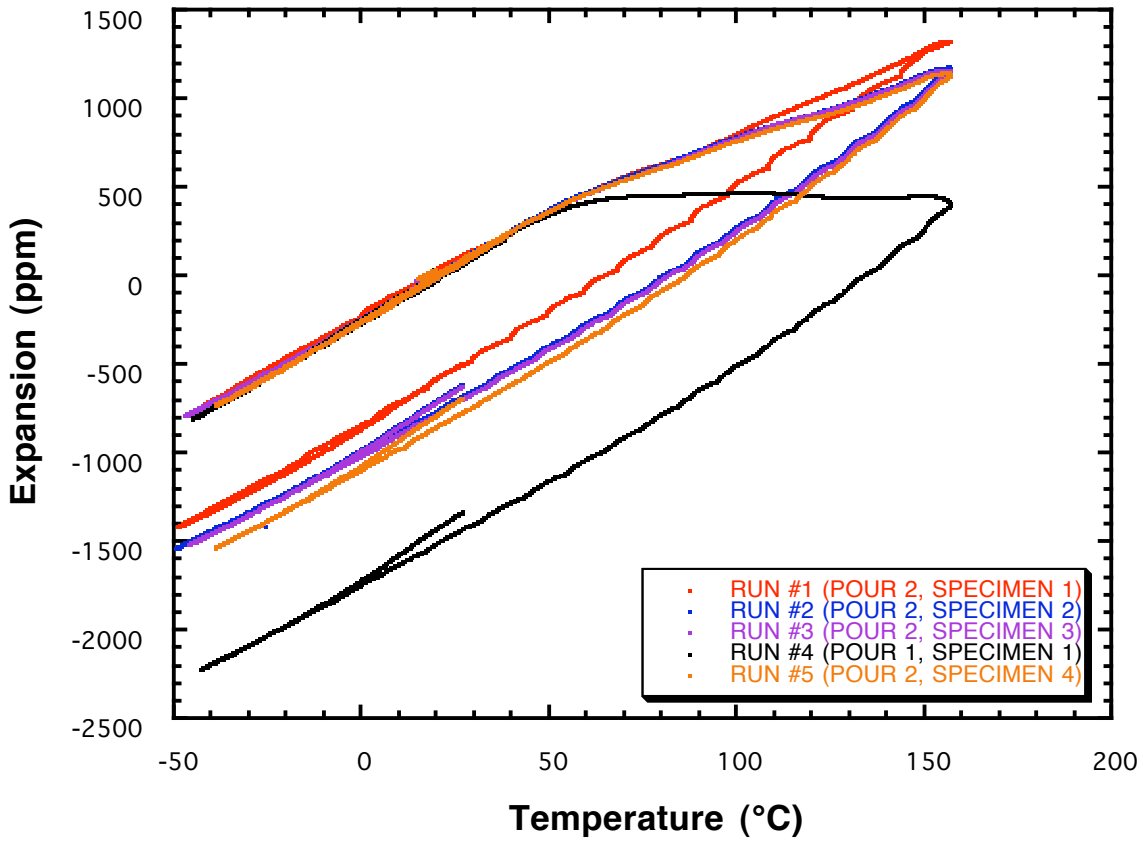

Fig. 6. Thermal expansion of Type 277-4 cement material as a function of temperature.

Table 4. Measured thermal expansion values and Mean CTE for Type 277-4 specimens

Temperature, °C	Run #1		Run #2		Run #3		Run #4		Run #5	
	exp, ppm	MCTE, ppm/°C	exp, ppm	MCTE, ppm/°C	exp, ppm	MCTE, ppm/°C	exp, ppm	MCTE, ppm/°C	exp, ppm	MCTE, ppm/°C
-40	-741	12.4	-727	12.1	-725	12.1	-759	12.6	-753	12.6
-20	-517	12.9	-500	12.5	-498	12.4	-519	13.0	-520	13.0
0	-266	13.3	-251	12.6	-247	12.3	-251	12.5	-260	13.0
20	0		0		0		0		0	
40	239	12.0	252	12.6	245	12.3	240	12.0	248	12.4
60	463	11.6	466	11.6	455	11.4	410	10.2	458	11.5
80	628	10.5	622	10.4	611	10.2	448	7.5	605	10.1
100	797	10.0	778	9.7	772	9.7	465	5.8	757	9.5
120	983	9.8	907	9.1	905	9.1	447	4.5	882	8.8
140	1166	9.7	1050	8.8	1042	8.7	434	3.6	1019	8.5
150	1271	9.8	1136	8.7	1126	8.7	449	3.4	1108	8.5

The expansion data in the interval -40 to 150°C for 3 of the Lot 2 specimens (Run #2, #3 and #5) were pooled and then sorted in ascending order by temperature. A moving average smoothing routine with a 31-point window (corresponds to less than 1°C temperature interval) was used to smooth both the temperature and expansion data. A cubic spline fit through this pooled, sorted and smoothed data set was then used to generate values for the expansion at increments of 1°C as shown in Table 5. The spline fit indicated an expansion of 1.6 ppm at 20°C. Since by definition the expansion is zero at the 20°C reference temperature, the values of Table 5 have been offset by this amount.

Table 5. Expansion values at even intervals estimated from cubic spline fit of pooled, sorted and smoothed data from Runs 2, 3, and 5.

TEMPERATURE, °C	ESTIMATED EXPANSION, ppm	ESTIMATED MCTE, ppm/°C	TEMPERATURE, °C	ESTIMATED EXPANSION, ppm	ESTIMATED MCTE, ppm/°C
-37	-706	12.4	5	-190	12.7
-36	-695	12.4	6	-177	12.7
-35	-683	12.4	7	-165	12.7
-34	-671	12.4	8	-152	12.7
-33	-661	12.5	9	-139	12.7
-32	-649	12.5	10	-126	12.7
-31	-638	12.5	11	-114	12.7
-30	-625	12.5	12	-101	12.7
-29	-614	12.5	13	-88	12.7
-28	-603	12.6	14	-76	12.7
-27	-591	12.6	15	-63	12.6
-26	-578	12.6	16	-50	12.6
-25	-567	12.6	17	-37	12.6
-24	-555	12.6	18	-25	12.6
-23	-544	12.7	19	-12	12.6
-22	-532	12.7	20	0	12.6
-21	-519	12.7	21	12	12.6
-20	-508	12.7	22	25	12.6
-19	-496	12.7	23	38	12.7
-18	-484	12.7	24	50	12.6
-17	-470	12.7	25	63	12.6
-16	-458	12.7	26	75	12.6
-15	-446	12.8	27	88	12.6
-14	-433	12.8	28	100	12.6
-13	-420	12.8	29	113	12.6
-12	-408	12.8	30	125	12.5
-11	-395	12.7	31	137	12.5
-10	-382	12.8	32	150	12.5
-9	-369	12.7	33	162	12.5
-8	-356	12.7	34	174	12.5
-7	-344	12.7	35	186	12.4
-6	-331	12.7	36	198	12.4
-5	-317	12.7	37	210	12.4
-4	-304	12.7	38	222	12.4
-3	-292	12.7	39	235	12.4
-2	-279	12.7	40	246	12.3
-1	-267	12.7	41	258	12.3
0	-254	12.7	42	270	12.3
1	-241	12.7	43	281	12.3
2	-228	12.7	44	293	12.2
3	-216	12.7	45	305	12.2
4	-203	12.7	46	316	12.2

Table 5. (Continued)

TEMPERATURE, °C	ESTIMATED EXPANSION, ppm	ESTIMATED MCTE, ppm/°C
47	327	12.1
48	338	12.1
49	349	12.1
50	360	12.0
51	371	12.0
52	381	11.9
53	392	11.9
54	402	11.8
55	412	11.8
56	421	11.7
57	431	11.7
58	440	11.6
59	449	11.5
60	458	11.5
61	466	11.4
62	475	11.3
63	483	11.3
64	492	11.2
65	500	11.1
66	508	11.0
67	515	11.0
68	523	10.9
69	530	10.8
70	538	10.8
71	545	10.7
72	552	10.6
73	559	10.6
74	566	10.5
75	573	10.4
76	581	10.4
77	588	10.3
78	596	10.3
79	603	10.2
80	611	10.2
81	619	10.1
82	626	10.1
83	634	10.1
84	642	10.0
85	650	10.0
86	658	9.98
87	666	9.94
88	673	9.91
89	681	9.88
90	689	9.86
91	697	9.83
92	705	9.79
93	713	9.78
94	720	9.74
95	728	9.72
96	736	9.69
97	744	9.67
98	752	9.64
99	759	9.62
100	767	9.60
101	776	9.58
102	783	9.55
103	790	9.53
104	797	9.50
105	804	9.46
106	812	9.44
107	818	9.40
108	825	9.38
109	831	9.34
110	837	9.31
111	844	9.28
112	850	9.25
113	856	9.21
114	862	9.18
115	867	9.13
116	873	9.10
117	879	9.06
118	885	9.03
119	890	8.99
120	897	8.97
121	902	8.94
122	908	8.91
123	914	8.88
124	920	8.85
125	926	8.82
126	933	8.81
127	939	8.78
128	946	8.76
129	953	8.74
130	959	8.72
131	966	8.71
132	974	8.70
133	980	8.68
134	987	8.67
135	996	8.66
136	1003	8.65
137	1011	8.64
138	1019	8.64
139	1026	8.63
140	1034	8.62
141	1043	8.62
142	1051	8.62
143	1059	8.62
144	1068	8.62
145	1076	8.62
146	1085	8.62
147	1094	8.62
148	1104	8.63
149	1113	8.64
150	1122	8.63

Figure 7 compares the pooled experimental expansion data with the smoothed data and the cubic spline fit. The relative residuals of the spline fit are shown in Fig. 8. It can be seen that the estimated expansion values from the spline fit are within 0.2% of the smoothed data.

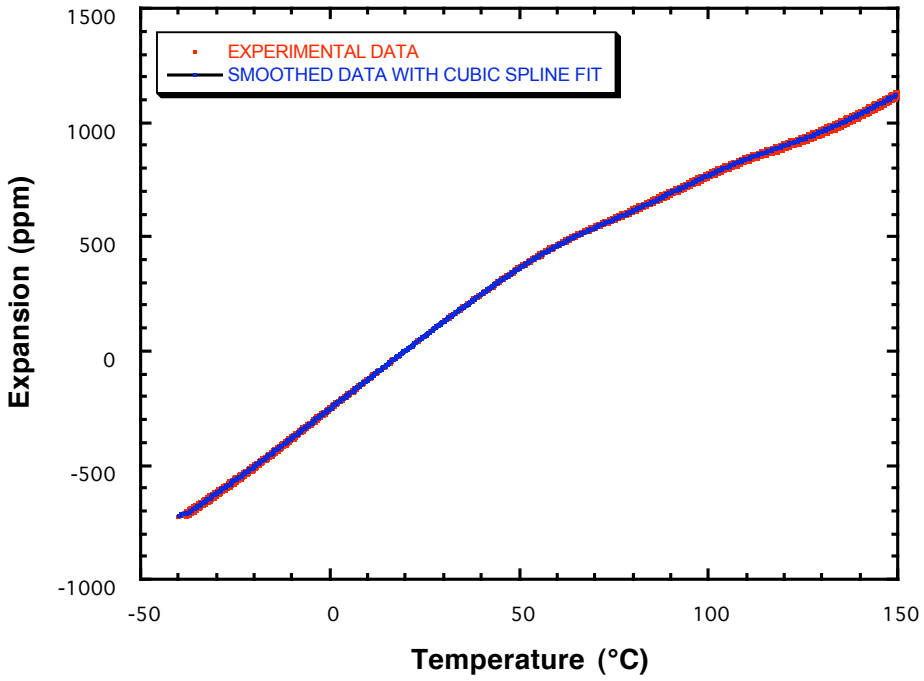

Fig. 7. Comparison of smoothed data and cubic spline fit of smoothed data to raw pooled experimental data for thermal expansion of Type 277-4 cement material as a function of temperature.

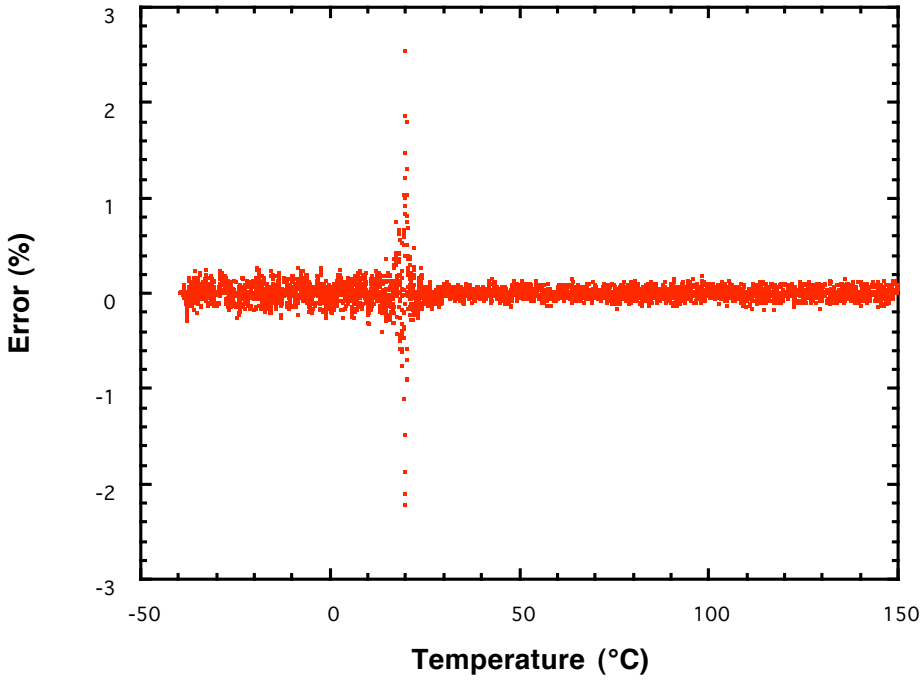

Fig. 8. Relative residuals of cubic spline fit used to estimate expansion values tabulated in Table 5.

The estimated expansion at the 1°C increments was used to calculate the MCTE values shown in Table 5. The value of MCTE at 20°C cannot be calculated because of a division by zero condition; therefore, the average of the 19 and 21°C MCTE values is listed in Table 5. Figure 9 shows a plot of the MCTE values from Table 5 along with a 9th order polynomial used to fit the values. The MCTE at any temperature in the range -37 to 150°C can be calculated using

$$\begin{aligned}\text{MCTE (ppm/°C)} = {} & 12.699164 - 0.0073715235*T + 0.00018778752*T^2 \\ & + 1.517514e\text{-}05*T^3 - 6.6945913e\text{-}07*T^4 - 2.4414824e\text{-}09*T^5 \\ & + 2.7529257*T^6 - 3.4686036e\text{-}12*T^7 + 1.7626873e\text{-}14*T^8 \\ & - 3.2800845e\text{-}17*T^9 \end{aligned} \quad (2)$$

It is strongly cautioned that Eq. (2) cannot be used to extrapolate MCTE values outside the measured range and describes the behavior only during an initial heating. Figure 10 shows the relative residuals for Eq. (2) using 8 significant digits for the polynomial coefficients compared to the MCTE values from Table 5. It can be seen that Eq. (2) generates the MCTE values of Table 5 to within better than 1% over the temperature range measured in this study.

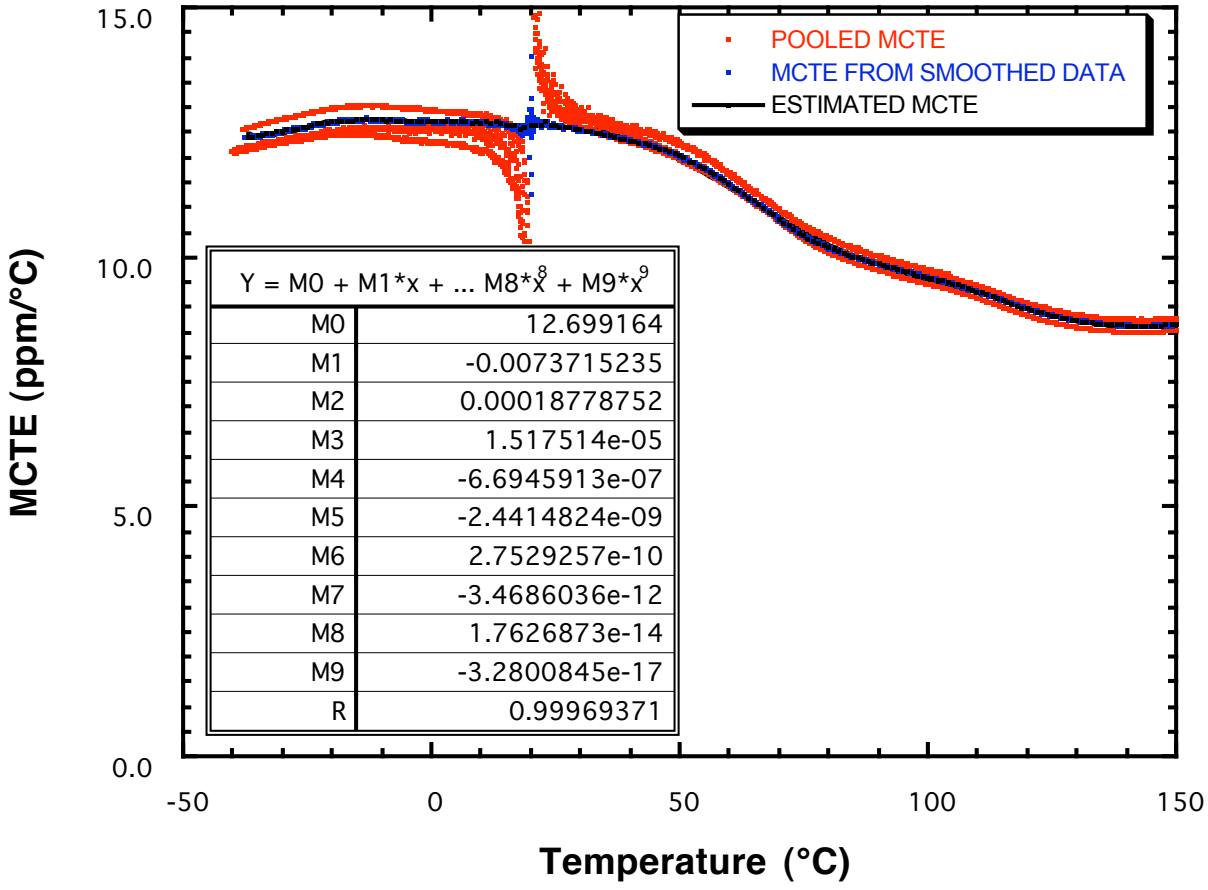

Fig. 9. Comparison of MCTE calculated from estimated expansion with MCTE calculated from smoothed expansion data and raw pooled MCTE values. Also shown is a 9th order polynomial fit of the MCTE calculated from the estimated expansion values of Table 5.

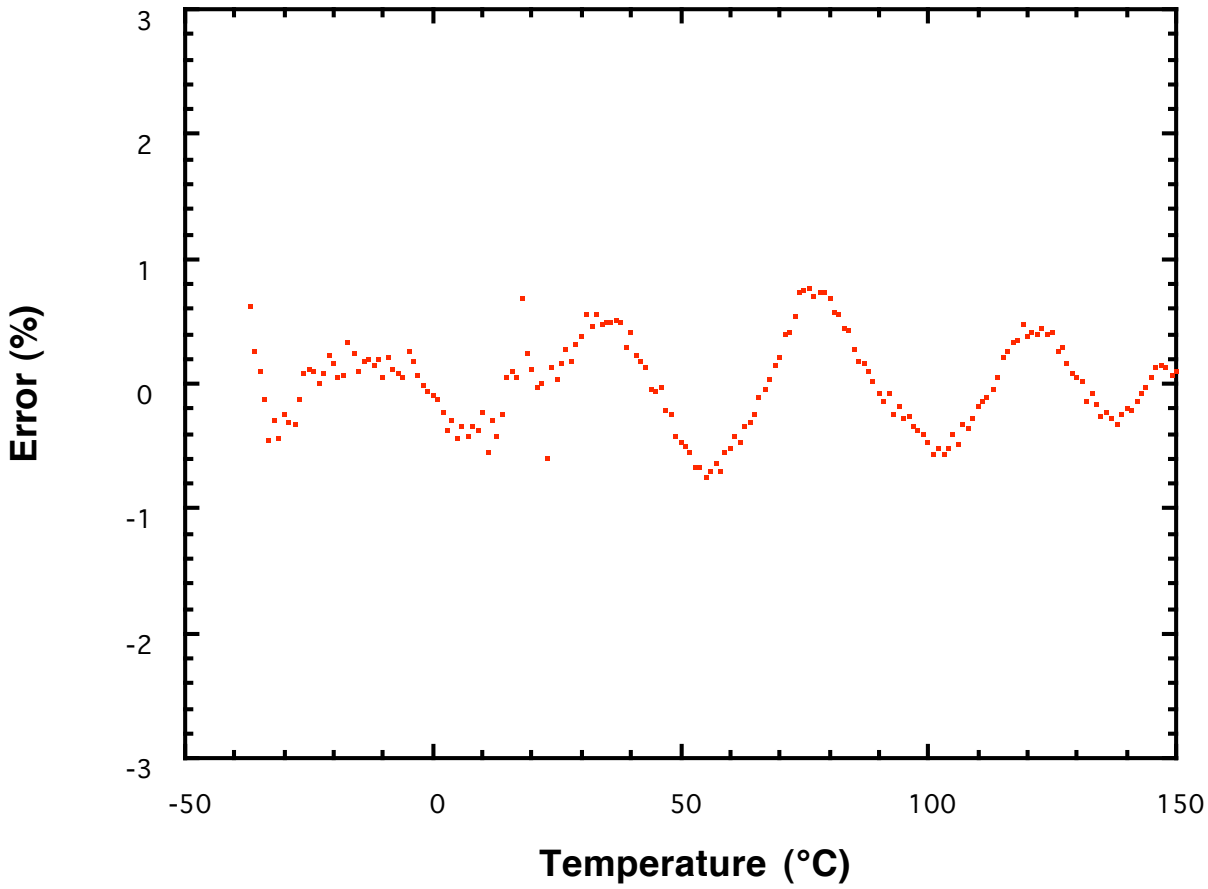

Fig. 10. Relative residuals of the 9th order polynomial fit of the estimated MCTE values using 8 significant digits for the coefficients as shown in Eq. (2).

After non-reversible behavior was demonstrated by the first specimen tested, the remaining four specimens were weighed before and after the expansion testing to determine any changes in mass resulting from heating the specimens. All specimens exhibited a weight loss of ~1.3% with individual results shown in Table 6. The initial density for the specimens tested is listed in Table 7. The Lot 1 specimen (Run #4) appeared to have a higher density than the Lot 2 specimens.

Table 6. Weight loss (%) behavior during testing

Run #1 (Lot 2, Specimen 1)	Not measured
Run #2 (Lot 2, Specimen 2)	-1.39
Run #3 (Lot 2, Specimen 3)	-1.24
Run #4 (Lot 1, Specimen 1)	-1.29
Run #5 (Lot 2, Specimen 4)	-1.34

Table 7. Initial density (10^6 g/m^3) of specimens tested

Run #1 (Lot 2, Specimen 1)	Not measured
Run #2 (Lot 2, Specimen 2)	1.47
Run #3 (Lot 2, Specimen 3)	1.50
Run #4 (Lot 1, Specimen 1)	1.60
Run #5 (Lot 2, Specimen 4)	1.48

4. SUMMARY

Two thermophysical properties, thermal conductivity and volumetric specific heat, were measured using the Hot Disk® method. The results among three random pairs of samples are consistent. All the specimens exhibited the same variations as a function of temperature.

The thermal expansion behavior was determined using a push rod dilatometer. Two specimens were considered to be outliers. Data from the remaining 3 specimens were pooled and the MCTE was described by a 9th order polynomial equation to within 1%.

All specimens lost about 1.3% during the expansion testing. Measured density of the specimens was found to be about $1.50*10^6$ g/m^3 for Lot 2 and about $1.60*10^6$ g/m^3 for Lot 1.

Since the material tested in this study undergoes irreversible changes the first time it is heated above 50°C, the data reported is valid only for the first time the material is heated above 50°C and must not be used to describe subsequent heating cycles.

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