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NON-METALLIC THERMAL STORAGE MEDIA

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MINERAL PROCESSING DIVISION

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Mines Branch Research Report R 96

NON-METALLIC THERMAL STORAGE MEDIA

by

V. D. Svikis*

SYNOPSIS

To evaluate their suitability as thermal storage media, seven ceramic products, thirteen ceramic bodies, twenty-two rocks and fifteen ceramic-rock bodies -- all low-cost non-metallics -- were submitted to determinations of thermal properties such as specific heat and heat capacity per unit volume. For this work a large calorimeter and a special electric furnace were designed and constructed.

The mean specific heat determinations were made by the method of mixtures in a calorimeter, using water. The procedure is described in detail. The heat capacities per unit volume were calculated from the densities and mean specific heats of the materials examined. The results are summarized and tabulated.

The results indicate that 'highly calcined' pure alumina (over 99% Al_2O_3) and dead-burned magnesia (over 93% MgO) have the best heat capacities of the ceramic products and rocks examined. Two-, three-, and four-component bodies from ceramic products or ceramic products and rocks, bonded with Ciment Fondu, are economically more attractive but have lower heat capacities than calcined alumina and dead-burned magnesia. However, bodies consisting of dead-burned magnesite clinker, fireclay brick, and building brick are adequate thermal storage media. In certain cases, the fireclay brick and the building brick in these body compositions can be successfully replaced by rocks, such as sandstone, quartzite, and granite.

It is concluded that materials and material compositions rich in dead-burned magnesia are excellent low-cost thermal storage media. Although pure alumina has high heat capacity, its cost is almost twice that of dead-burned magnesia, making it expensive for use as a thermal storage medium.

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Direction des mines

Rapport de recherches R 96

SUBSTANCES NON MÉTALLIQUES CONVENANT À L'EMMAGASINAGE DE LA CHALEUR

par

V.D. Svikis*

RÉSUMÉ

Aux fins de déterminer la capacité d'absorption de la chaleur de certains minéraux, on a mesuré certaines valeurs techniques telles que la chaleur spécifique et la capacité calorifique par unité volumétrique dans le cas de sept produits céramiques, treize pâtes céramiques, vingt-deux roches, et quinze pâtes constituées d'un mélange de matière tant céramique que rocheuse, tous ces matériaux non métalliques étant d'un coût peu élevé. On a, à cette fin, imaginé et construit un gros calorimètre et un four électrique spécial.

Les déterminations de la chaleur spécifique moyenne ont été faites suivant le procédé des mélanges dans un calorimètre, à l'aide de l'eau. Le procédé en question est décrit en détail. Le degré d'absorption thermique par unité volumétrique a été calculé en tenant compte des densités et des chaleurs spécifiques moyennes des matériaux examinés. Les résultats sont indiqués de façon sommaire et apparaissent sous forme de tableaux dans le présent rapport.

Les résultats démontrent que, de tous les produits céramiques et roches examinés, ce sont l'alumine pure (à plus de 99% en Al_2O_3) "calcinée à fond" et la magnésie (à plus 93% en MgO) calcinée à mort qui possèdent le plus haut degré d'absorption thermique. Des pâtes à deux, à trois et à quatre constituants, faites de produits céramiques, ou encore de produits céramiques et de roches, agglomérés au moyen de Ciment Fondu, sont plus intéressantes du point de vue économique, mais elles ont des capacités calorifiques inférieures à celles de l'alumine calcinée ou de la magnésie calcinée à mort. Toutefois, des pâtes constituées de clinker de magnésite calcinée à mort, de briques faites d'argile réfractaire et de

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briques de construction constituent des matériaux convenant bien à l'emmagasinage de la chaleur. Dans certains cas, la brique faite d'argile réfractaire et la brique de construction des pâtes susmentionnées peuvent être avantageusement remplacées par des roches telles que le grès, le quartzite et le granit.

L'auteur en conclut que les matériaux et les mélanges riches en magnésie calcinée à mort constituent d'excellentes substances absorbantes de la chaleur. Même si l'alumine pure possède une capacité calorifique élevéé, le coût en est près du double de celui de la magnésie calcinée à mort, de sorte que, en tant que matériau d'emmagasinage de la chaleur son prix de revient est élevé.

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INTRODUCTION

The electricity supply industry was born at the end of the nineteenth century. This was a period when industrial development was based on the utilization of cheap coal and steam. Electricity was considered to be too expensive for heating.

Since those days, particularly after World War II, electricity has become less expensive. It is no longer a luxury and is competitive in many industrial fields. Further reductions in the cost of electricity, relative to other fuels, will increase the demand for electrical space heating.

Electricity, as supplied to the public, is different from other fuels in that it cannot be stored. Electric power plants must be capable of handling maximum load at any time. The costs would be at a minimum if electric plants could be used to full capacity twenty-four hours a day. This cannot be achieved in practice, but load factors would be greatly improved if consumers could take supplies of electricity during the night at off-peak hours (1,2)*.

The use of off-peak electricity for heating is a logical development in power-station economy. To make electrical heating attractive to the consumer, running costs must be comparable with those of other fuels for equal comfort. Electric power companies and commissions in Canada, and in some other countries, are studying the possibilities of equalizing electric power demands between day and night, and are considering the granting of low household electricity

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* The references are listed numerically at the end of this report.

rates for off-peak hours. This problem will be especially important when nuclear power stations begin to produce electrical energy. Once the nuclear power station has been started and worked up to full load, the load should be steadily maintained. An adequate off-peak load should be ensured, otherwise the electrical energy available at the time of light load will have to be turned to waste, resulting in loss of efficiency and in increased costs.

An off-peak heating system must make use of a thermal storage medium. In older heating systems, soap-stone and even cast iron were used as storage media. Later, they were replaced by fire brick and building brick; dry sand was used to fill the smaller spaces between the bricks. Modern block-type heaters are filled with ordinary building brick without sand, or blocks are made of concrete or fireclay(1). When such blocks are heated by properly designed electrical heating elements to about 800°F, they store electrically-generated heat. The blocks, or batteries of blocks, can be economically heated at night by utilizing low rate off-peak-hour electricity. During the day, when industry and households require electric power at a great rate, these thermal storage block heaters can discharge the accumulated heat. Thus, low rate off-peak-hour electrical energy can be economically used to heat not only most commercial and industrial premises but also private houses.

The idea of storing electrically-generated heat is relatively old. Electric thermal storage block heaters are quite popular in Europe, probably owing to the general use of the closed stove for space heating.

SCOPE OF RESEARCH

The work described in this report was undertaken to develop non-metallic thermal storage media that can be used in the form of blocks. Their principal requirements are high heat capacity and economic production costs. Accordingly, ceramic products, rocks, and similar materials of low cost were selected and examined to meet these requirements.

Special equipment, consisting of a large-capacity water calorimeter and a well insulated muffle furnace, was designed and constructed for this investigation.

The mean specific heats and the densities of the selected materials were determined. The determinations were carried out on single materials and on material compositions.

The data obtained were used to calculate and compare the heat capacities of the different materials and their compositions, and to determine their value as thermal storage media.

REVIEW OF LITERATURE ON SPECIFIC HEATS OF CERAMIC PRODUCTS AND ROCKS

The literature covering the specific heats of ceramic products and rocks indicates that much research has been devoted to the ceramic materials and products, particularly to refractories. Fewer data are available on the specific heats of rocks and minerals.

Wilson, Holdcroft and Mellor(3) determined the specific heat of the fireclay brick up to 1300°C. They showed that the specific heat increases quite rapidly with temperature. Bradshaw and

Emery(4) used a similar method, and obtained specific heats for fireclay brick up to 1400°C. Heyn, Bauer and Wetzel(5) made an extensive investigation into specific heats and provided data on four firebricks. In addition to these investigators, Tadokoro(6) carried out an extensive series of investigations on the thermal properties of refractories. He obtained specific heat values for fireclay brick up to 900°C. MacGee(7) in his work reported on five fireclay bricks.

Commercial magnesite and magnesite brick have been studied and reported by Heyn, Bauer and Wetzel(5), Tadokoro(6), Green(8, 9), and some others. Wilkes(10) has determined specific heats on chemically pure magnesium oxide and aluminum oxide over a range of temperature extending from 20° to 1800°C. Seil, Heck and Heiligman(11) investigated magnesite ores and reported specific heats between 25° and 850°C.

Determinations of the specific heat of chrome ores and chrome bricks have been made by Tadokoro(6) and by Seil, Heck and Heiligman(11).

The specific heats on silica bricks have been studied by Tadokoro(6), Heyn, Bauer and Wetzel(5), and Bradshaw and Emery(4). The results of their work indicate that there is little difference between the specific heats of silica and fireclay products.

Ceramic materials and products, such as clays, quartz, sillimanite, zirconia, building brick, insulation brick, etc., have been investigated, and their specific heats reported, by Knote(12), Navias(13), Cohn(14), MacGee(7), White(15, 16), Winkler(17), and others.

Few references on the specific heats of minerals and rocks are found in the literature. Tadokoro(6) studied the specific heats of a large number of different rocks at temperatures up to 100°C. White(16) examined the specific heats of selected minerals over a wide range of temperatures. His work is considered in the literature to be one of the most accurate.

A survey of the literature reveals a lack of systematic and complete information. Different authors have used different methods for the determination of specific heats. The ranges of temperature over which the mean specific heats are determined by different investigators also vary. It is quite difficult to make a comparison of the data given by several authors. In many cases there is an absence of information concerning physical characteristics of the materials investigated.

In view of all this and of the specific requirements of this project, it was realized that the specific heats of the selected ceramic products and rocks, and particularly of their body compositions, should be determined.

MATERIALS INVESTIGATED

Low-cost commercial ceramic products and certain types of rocks were selected as non-metallic materials for this project.

The selection of high-heat-capacity ceramic products was chiefly based on data found in the literature covering the specific heats of refractory materials.

Because the literature on the specific heats of rocks is sparse, some preliminary specific heat determinations were run prior to the selection of the types of rocks to be used.

Ceramic Products

The following commercial ceramic products were used for this investigation:

	Product	Composition
(1)	High alumina brick	99.42% Al_2O_3
(2)	Periclase brick	93.0% MgO
(3)	Magnesite brick	85.0% MgO
(4)	Silica brick	94.5% SiO_2
(5)	Graphite brick	Unknown
(6)	Fireclay brick	37.0% Al_2O_3, 60.0% SiO_2
(7)	Building brick	Absorption 8%; 56.0% SiO_2, 16.0% Al_2O_3
(8)	Magnesite clinker (dead-burned)	95.4% MgO
(9)	Chrome-magnesite brick (crushed)	70.0% Cr_2O_3, 30.0% MgO
(10)	Silicon carbide, -35 mesh	
(11)	Ciment Fondu*	High alumina cement

Commercial ceramic products from (1) to (5) were investigated chiefly as single materials. Ceramic products from (6) to (10) were employed as constituents in ceramic bodies. Ciment Fondu was employed chiefly as a binder in body compositions; it was, however, considered as one of the body constituents in all bodies made from ceramics and rocks.

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* Ciment Fondu Lafarge (Canada) Ltd., Montreal, Canada.

Types of Rocks

Twenty-two Canadian rock types, having distinctive structures, textures or compositions, were selected for the investigation. A petrographic study of the rocks was made by Soles(18) in the laboratories of the Mines Branch, and complete descriptions are available in separate reports. A brief summary is included here, in Tables 1 and 2.

The majority of rocks were investigated as single materials. Magnesian limestone M-187, Dolostone M-186, Sandstone M-176, Quartzite M-207, "Quartz Rock" M-179, Granite M-195, and Dolostone M-168 were selected and employed as constituents in ceramic-rock bodies. In this work the term 'Dolostone' refers to a type of rock which has the mineral dolomite as its principal component.

Body Compositions

The ceramic bodies consisted of two and three ceramic components. Identifications of the ceramic bodies and their respective compositions are given in Tables 3 and 4.

TABLE 1

Classifications and Compositions of Selected Rocks

Sample		Mineral Composition, %					Texture	Gross Structure
Rocks	No.	Quartz	K-Feldspar	Na-Feldspar	Ca-Feldspar	Ferromagnesians and Miscellaneous		
Albite Granite	M-195	29	21	45	-	3, Biotite; 2, Muscovite	Hypidiomorphic, medium-grained	Homogeneous
Anorthosite	M-193	-	1	-	97 (An_{50})	1, Augite; 1, Magnetite	Hypidiomorphic, coarse-grained	Homogeneous
Sandstone	M-176	92	8	-	-	- -	Sugary, fine-grained	Slight banding
Gabbro (Diabasic)	M-178	←------- 12 (Graphic) -------→			46 (An_{50})	24, Augite; 71, Hornblende, Biotite; 7, Magnetite	Diabasic, medium-grained	Homogeneous
Nepheline Syenite	M-188	-	23	52	-	2, Magnetite; 23, Nepheline	Hypidiomorphic, medium-grained	Homogeneous
Basalt	M-189	←------------ 23 ------------→				42, Epidote; 20, Augite; 10, Chlorite; 5, Magnesite	Fine-grained, altered	Irreg. banded
Rhyolite	M-190	23	52	21	-	3, Magnetite	Allotriomorphic, medium-grained	Homogeneous
Syenite	M-191	-	69(Perthite)	17	-	9, Hornblende; 2, Biotite; 3, Magnetite	Hypidiomorphic, medium-grained	Homogeneous
Nordmarkite	M-192	9	73(Perthite)	8	-	7, Hornblende; 2, Augite; 1, Magnetite and Hematite	Panidiomorphic coarse-grained	Homogeneous
"Graywacke"	M-199	25	(Inc. feldspar ?)			70, Hornblende; 5, Calcite	Metamorphic, medium-grained	Banded, gneissic
"Iron-Formation"	M-200	60	-	-	-	23, Grunerite; 17, Magnetite	Metamorphic, medium-grained	Banded, gneissic
Granite	M-194	34	31	31	-	3, Biotite	Hypidiomorphic, medium-grained	Homogeneous
Granodiorite	M-208	21	4	-	51 (An_{30})	12, Hornblende; 9, Biotite; 3, Epidote and Sphene	Hypidiomorphic, medium-grained	Homogeneous
Granite	M-209	33	29	23	-	10, Biotite	Hypidiomorphic, medium-grained	Homogeneous
Quartz Monzonite	M-210	27	20	-	42 (An_{28})	10, Biotite; 1, Muscovite	Panidiomorphic, coarse-grained	Homogeneous
"Quartz Rock"	M-179	100	-	-	-	- -	Coarse crystals	Massive
Quartzite	M-207	93	-	-	-	7, Muscovite	Strained, fine-grained	Locally foliated

(After J. A. Soles (18))

TABLE 2

Classifications and Compositions of Selected Carbonate Rocks

Sample		Mineral Composition, %			Texture	Gross Structure
Rocks	No.	Calcite	Dolomite	Others		
Limestone	M-184	94	4	2, Clay	Sedimentary, fine-grained	Locally banded
Limestone	M-185	88	10	1, Diopside, Quartz, Graphite	Recrystallized, coarse-grained	Homogeneous
Magnesian Limestone	M-187	72	27	1, Impurities	Fine-grained	Homogeneous (ex. fossils)
Dolostone	M-186	-	80	1, Sulphides and Oxides; 19, Voids	Medium-grained	Large voids
Dolostone	M-168	-	98	2, Tremolite	Coarse crystals	Homogeneous

(After J. A. Soles (18))

TABLE 3

Compositions of Bodies with Two Ceramic Components

Bodies	Magnesite Clinker, %	Chrome-Magnesite Brick, %	Fire-clay Brick, %	Building Brick, %	Silicon Carbide, %	Ciment Fondu, %
A1	75	-	-	-	-	25
A2	-	75	-	-	-	25
A3	-	-	75	-	-	25
A4	-	-	-	75	-	25
A5	-	-	-	-	75	25

TABLE 4

Compositions of Bodies with Three Ceramic Components

Bodies	Magnesite Clinker, %	Chrome-Magnesite Brick, %	Fire-clay Brick, %	Building Brick, %	Ciment Fondu, %
B1	25	50	-	-	25
B2	25	-	50	-	25
B3	25	-	-	50	25
B4	50	25	-	-	25
B5	50	-	25	-	25
B6	50	-	-	25	25
B7	-	25	50	-	25
B8	-	50	25	-	25

The ceramic-rock bodies consisted of two, three, and four ceramic and rock components. Identifications of the ceramic-rock bodies and their respective compositions are shown in Tables 5, 6 and 7.

TABLE 5

Compositions of Bodies with One Rock and One Ceramic Component

Bodies	Quartz-Rock M-179, %	Quartzite M-207, %	Sandstone M-176, %	Granite M-195, %	Magnesian Limestone M-187, %	Dolostone M-186, %	Dolostone M-168, %	Ciment Fondu, %
C1	75	-	-	-	-	-	-	25
C2	-	75	-	-	-	-	-	25
C3	-	-	75	-	-	-	-	25
C4	-	-	-	75	-	-	-	25
C5	-	-	-	-	75	-	-	25
C6	-	-	-	-	-	75	-	25
C7	-	-	-	-	-	-	75	25

TABLE 6

Compositions of Bodies with One Rock and Two Ceramic Components

Bodies	Magnesite Clinker, %	Quartzite M-207, %	Sandstone M-176, %	Granite M-195, %	Ciment Fondu, %
D1	50	25	-	-	25
D2	25	50	-	-	25
D3	50	-	25	-	25
D4	25	-	50	-	25
D5	50	-	-	25	25
D6	25	-	-	50	25

TABLE 7

Compositions of Bodies with Two Rock and Two Ceramic Components

Bodies	Magnesite Clinker, %	Sandstone M-176, %	Magnesian Limestone M-187, %	Granite M-195, %	Ciment Fondu, %
E1	25	25	25	-	25
E2	25	-	25	25	25

EXPERIMENTAL APPARATUS AND PROCEDURE

Preparation of Test Specimens

(i) From Ceramic Products and Rocks

All commercial ceramic products, with the exception of four, were received in the form of a brick. The rock samples had irregular sizes and shapes. Three test specimens, measuring 1½ in. x 1½ in. x 4 in., were cut from each brick and rock sample. A hole 1/4 in. in diameter was drilled along the 4-in. axis to the centre of each specimen. The hole served as a place in which to insert the thermocouple for measuring the temperature of the specimen during heating. It also facilitated more uniform and faster heating of the specimen, and, conversely, faster cooling within the calorimeter.

(ii) From Ceramic Bodies and Ceramic-Rock Bodies

Ceramic products and rocks, which were selected as aggregates for bodies, were crushed, screened and graded in the following grain sizes:

Mesh (Tyler)	%
- 8+20	50
- 20+65	15
- 65	35

Experimental bodies were prepared by mixing, in various proportions, graded aggregates and high-alumina hydraulic cement. The identifications and compositions of the bodies are shown in Tables 3, 4, 5, 6 and 7.

The blending of batch materials in the dry state was carried out in a small laboratory mixer for a period of five minutes. Each body was then tempered with the minimum amount of water (water-cement ratio approx. 0.5) to attain workable consistency. Test specimens were formed by tamping the material into 1½ in. x 1½ in. x 4 in. wooden moulds. The filled moulds were vibrated for a short period, and then the exposed surfaces of the cast specimens were covered with a glass sheet to prevent water evaporation. After setting for approximately 24 hours, the test specimens were removed from the moulds, maintained at room temperature for a further 24-hour period, and then dried at 110° C.

Three to four test specimens were prepared from each ceramic and ceramic-rock body. As was done for single materials, a hole 1/4 in. in diameter was drilled along the 4-in. axis to the centre of each specimen.

Determination of Mean Specific Heats

(i) Methods of Measurement

Heat capacity may be defined as the amount of heat required to raise by one degree the temperature of a given amount of a substance. To compare the thermal capacities of different substances, a standard measurement termed specific heat is used. It is defined as the quantity of heat required to raise the temperature of 1 g of a substance by 1°C(19). The units used to express specific heat are cal/g .°C.

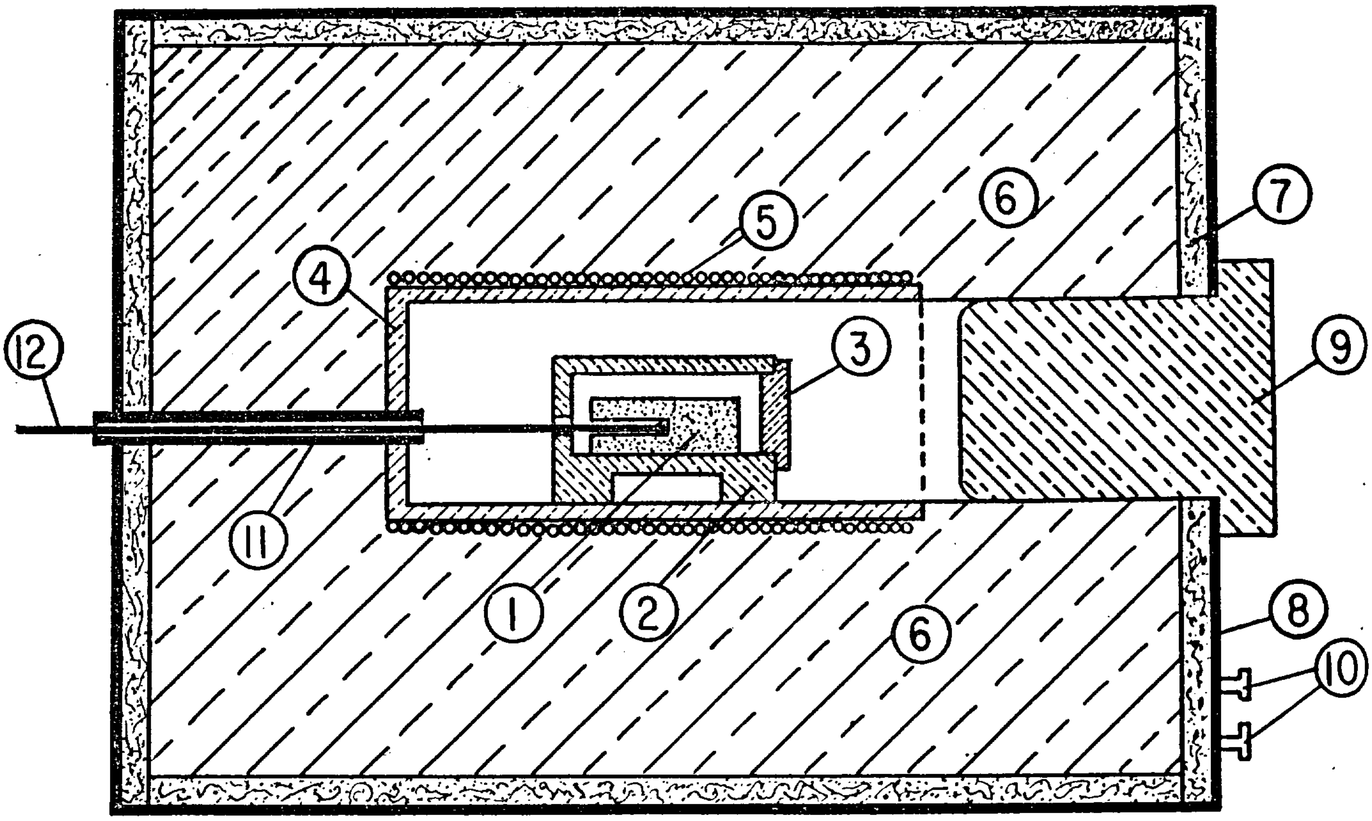
Specific heat, like density and thermal conductivity, is generally a function of temperature, and is almost never determined directly for any particular temperature. Specific heat is, essentially, the heat given out by a body in falling through a given temperature interval, divided by the interval. The result obtained is the mean specific heat for the interval (15).

The numerous methods which are employed for specific heat measurements can be divided into two categories, direct and indirect. With the direct method, the rise in temperature produced in the substance by a known amount of heat is measured. With the indirect method, the material is first heated to a known temperature in a furnace and then transferred to a calorimeter of known heat capacity. The heat content of the material is determined by measuring the rise in temperature of the calorimeter. This latter method is known as the "method of mixtures".

In the literature the method of mixtures is generally acknowledged to be the most suitable and accurate available for the determination of the specific heats of refractory products. Most of the available data on specific heats of ceramic products and rocks have been obtained by using various modifications of this method. For these reasons it was decided to use the method of mixtures for the determination of specific heats in this investigation.

(ii) Electric Furnace

The central part of the furnace, as shown in Figure 1, consisted of a high-temperature, grooved, refractory muffle having inside dimensions of 14 in. x 7½ in. x 5½ in. The muffle was wound externally with coiled 12 B & S gauge Chromel "A" (Cr 20%, Ni 80%) wire. The power consumption of the heating element was about 3.4 kilowatts at 115 volts. The muffle was set horizontally inside a transite box,



1. Test specimen
2. Ceramic container
3. Plug
4. Refractory muffle
5. Chromel "A" winding
6. Insulating brick
7. Asbestos sheet
8. Transite
9. Door (insul.brick)
10. Terminals
11. Mullite tube
12. Thermocouple

FIGURE I. ELECTRIC FURNACE.

which was supported by a steel frame. The transite box had an inside lining of 1-in. thick insulating block. The space between the muffle and this lining was densely packed with good quality insulating brick, to ensure uniformity of temperature within the muffle.

A 1/2-in. diameter hole was drilled through the back wall of the furnace and a mullite tube was inserted in the hole. An insulated chrome-alumel thermocouple was inserted through the mullite tube when the temperature within the furnace was to be measured.

A 5½ in. x 7½ in. opening was cut in the front of the furnace. A 6-in. thick, tightly-fitting door, that could be easily opened and closed, was fitted into the opening.

(iii) Calorimeter

The design of the water calorimeter used in this investigation was based chiefly on the description given by Seil, Heck and Heiligman(11). It consisted of a 12-in. diameter, 24-in. high glass jar having about 39,000 cm^3 capacity. The glass jar was covered with a 1/2-in. thick layer of felt and was inclosed in a wooden case measuring 22 in. x 22 in. x 31 in., as shown in Figure 2. The space between the felt-covered glass jar and the wooden case was filled with exfoliated vermiculite.

A removable lid on the top of the calorimeter was held tightly by several clamps. The central part of the lid was 3/4-in. thicker than the remainder. This part of the lid, in the form of a disc insulated with felt, fitted tightly into the jar when the lid was closed.

The stirring arrangement consisted of a glass shaft with two propellers inserted in a steel chuck. The shaft was driven by

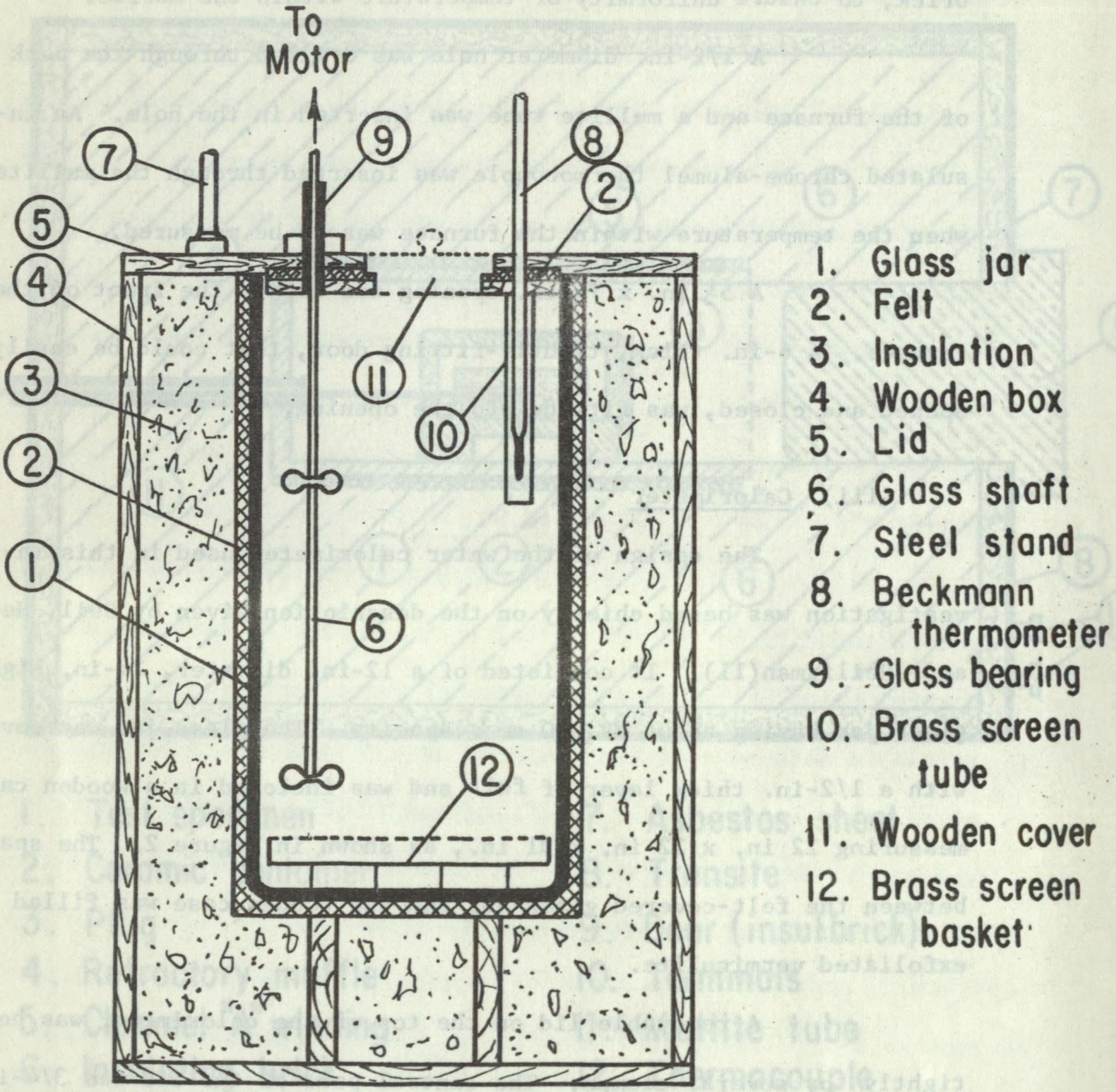


FIGURE 2. CALORIMETER.

a small electric motor. A steel stand, supporting the electric motor and a clamp with the Beckmann thermometer, was mounted on the lid. A glass bearing for the stirring shaft was fixed in a hole drilled through the lid. The lower part of the Beckmann thermometer in the calorimeter was protected by a tubular brass screen fastened underneath the lid.

The specimens were lowered into the calorimeter through a 4-in. square opening in the lid. The opening was kept closed by an insulated wooden cover, which was removed only for a short period when the specimen was dropped into the calorimeter.

A brass screen basket was located at the bottom of the glass jar to prevent damage to the jar when the specimen was dropped. The basket also ensured free circulation of the water around the specimen.

(iv) Heat Capacity of the Calorimeter

The average heat capacity of the calorimeter, in calories per degree centigrade, was determined as accurately as possible to ensure reliable results in later determinations. Initially, 34,000 ml of distilled water was measured and transferred to the calorimeter jar. The level of the water was accurately marked. Later, after each determination, the water level in the calorimeter was carefully checked by means of a specially designed level indicator. The level indicator consisted of a float with a needle and scale, and this was inserted in the calorimeter through the 4 in. x 4 in. opening in the lid.

The water in the calorimeter was stirred for about fifteen minutes, during which time the temperature was read on a Beckmann thermometer every minute. When the rate of temperature change remained constant for ten minutes, an empty, thin-walled copper cylinder heated to 60°C was quickly lowered into the calorimeter. The stirring of the water was continued and the temperature was read every minute. The readings were discontinued when the rate of temperature change remained constant for about twenty minutes. A time-temperature curve, as shown in Figure 3, was drawn and the rise in temperature of the calorimeter system, due to the insertion of the empty copper cylinder, was obtained. After twelve determinations the average rise was 0.044°C.

Next, the copper cylinder was sealed at one end and filled with a weighed quantity (about 1000 g) of distilled water. The cylinder and water were heated to 60°C in water bath. The water in the calorimeter was stirred again and the temperature was read on the Beckmann thermometer every minute. When the rate of temperature change remained constant for 10 minutes, the copper cylinder with water at 60°C was inserted quickly into the calorimeter. With the stirrer continually working, temperature readings were taken every minute with the Beckmann thermometer. The operation was discontinued when the rate of temperature change became constant for about twenty minutes. The time-temperature curve was plotted as shown in Figure 4.

Examination of the curve shows that as soon as the cylinder containing water at 60°C was inserted into the calorimeter the temperature rose rapidly, reached a maximum, then fell almost linearly. The correct temperature rise was obtained graphically when the curves showing the constant rates of change before and after insertion of the cylinder with water were projected. Fifteen determinations of the rise in temperature of the calorimeter system, due to the insertion of the copper cylinder containing about 1000 g of distilled water at 60°C, were carried out.

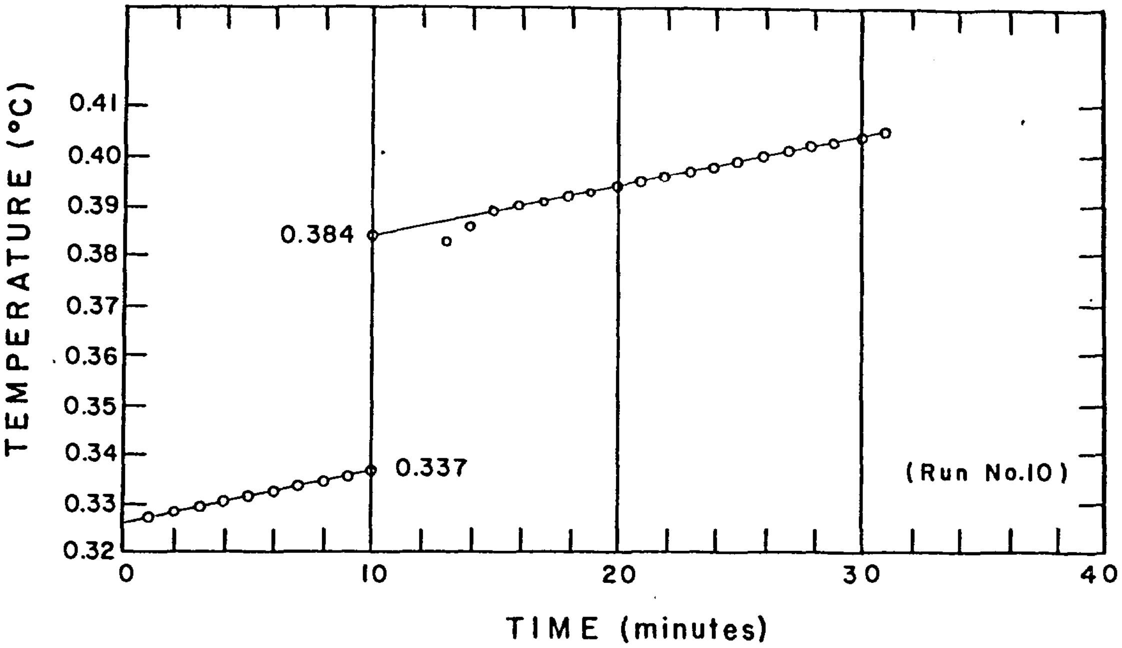


Figure 3. Time-Temperature Curve; Copper Cylinder at 60°C.

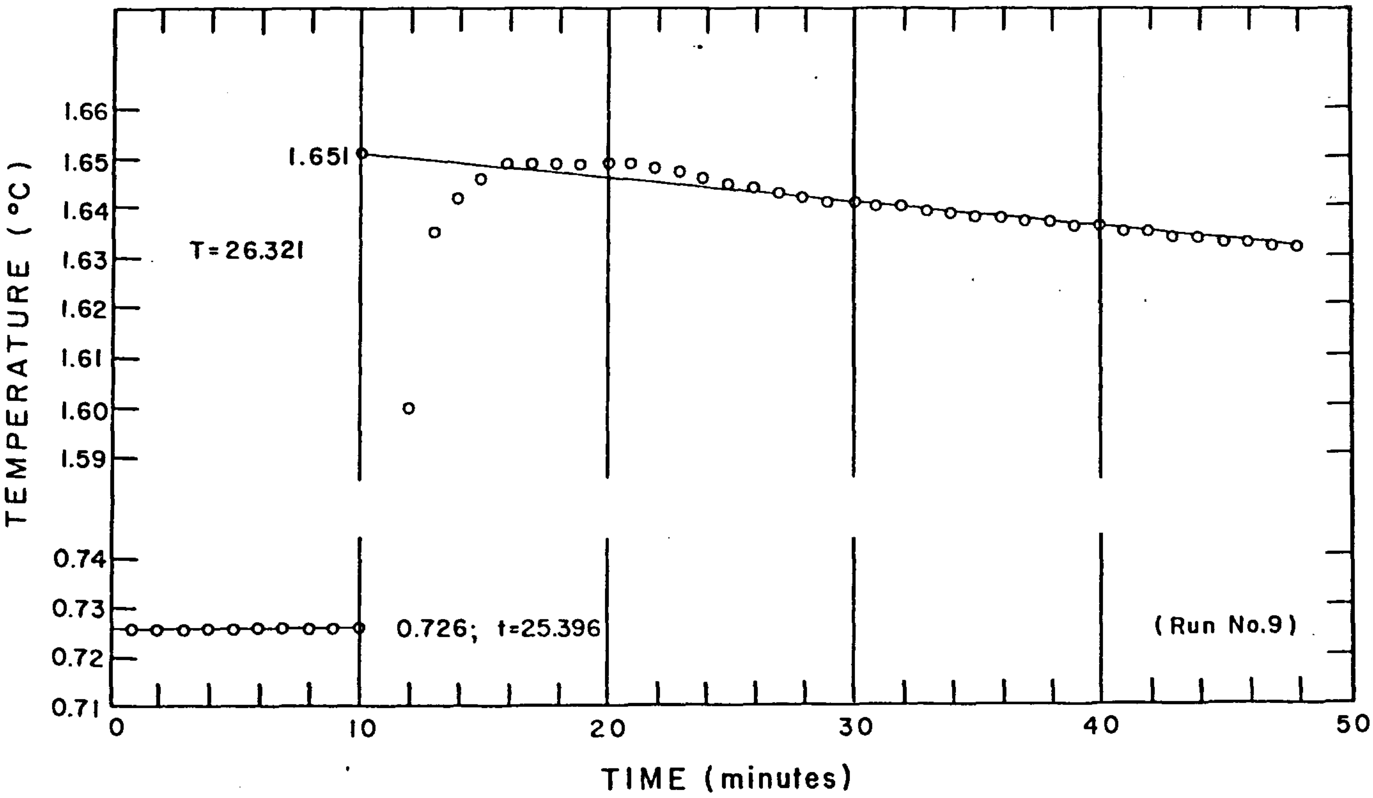


Figure 4. Time-Temperature Curve; Copper Cylinder with Water at 60° C.

The heat capacity of the calorimeter system was calculated after each determination, by the formula given below:

$$S = \frac{C\ W\ (60-T)}{T-t},$$

where:

C = specific heat of water at 60°C,
W = weight of water,
T = final temperature of calorimeter system,
t = initial temperature of calorimeter system, and
S = heat capacity of calorimeter system.

In all calculations the T value was corrected by 0.044°C, the rise in temperature due to the empty copper cylinder alone.

The average heat capacity of the calorimeter system was found to be 35,740 calories per degree C. This value was used in the specific heat determinations of the single ceramic products, the A and B ceramic bodies, and the single rocks. Later, when the glass jar of the calorimeter, accidentally broken, was replaced by a new one, the heat capacity of the calorimeter was re-determined. The new average heat capacity of the calorimeter was found to be 38,000 calories per degree C. This latter value was used in the specific heat determinations of the C, D and E ceramic-rock bodies.*

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* Details of these determinations are shown later in this report, under "Results and Discussion", as follows: Single ceramic products, Table 8 on page 28; A and B ceramic bodies, Tables 9 and 10 on pages 28 and 29; single rocks, Tables 11 and 12 on pages 32 and 33; and C, D and E ceramic-rock bodies, Tables 13, 14 and 15 on pages 33 and 36.

(v) Procedure for Determination of Mean Specific Heats

A weighed specimen, on which the specific heat was to be determined, was put in a 6 in. x 3 in. x 3 in. ceramic container. The container had 1/4-in. thick walls and was made from insulating brick. It was closed by a ceramic plug and placed in the middle of the muffle in the furnace as shown in Figure 1.

The temperature within the furnace was measured by means of a calibrated chromel-alumel thermocouple. It was inserted into the thermocouple hole of the specimen, through a small opening in the ceramic container, as shown in Figure 1. The cold junction of the thermocouple was kept in a Dewar flask containing an ice-water mixture. A Leeds and Northrup portable potentiometer was used that could be read directly to 0.01 millivolt.

Before the specimen was inserted, the furnace was heated up to about 430°C. It was maintained at this temperature constantly, except when a specimen was placed in the furnace. At that time the temperature of the furnace was slowly raised from 430°C to 456°C for the ceramic products, the A, B, C, D, and E bodies, and five rock samples; and from 430°C to 625°C for seventeen rock samples. In order to maintain the maximum uniformity of heat distribution within the specimen, the furnace was maintained at both top temperatures for at least one hour. Towards the end of this period the water in the calorimeter was stirred and the temperature observed on the Beckmann thermometer every minute. When the rate of change in temperature was constant in the calorimeter for ten minutes, the specimen was quickly transferred from the furnace to the calorimeter. In this operation the ceramic container holding the specimen was lifted from the furnace, the plug of the container was removed, and the specimen was quickly dropped into the calorimeter. The whole procedure required about six seconds. With continuous stirring of water in the calorimeter, the rise in temperature of the water was noted at one-minute intervals. When the rate of temperature change remained constant for about twenty minutes, temperature readings were discontinued and a time-temperature curve was plotted. A typical curve is shown in Figure 5.

The specific heat of the specimen was calculated from the rise in temperature of the water in the calorimeter, the heat capacity of the calorimeter system, and the weight and temperature of the specimen. In each case the mean specific heat between the temperature T_s and T was calculated by the following formula:

$$C = \frac{S\ (T-t)}{W_s\ (T_s - T)},$$

where:

S = heat capacity of calorimeter system,
T = final temperature of water in calorimeter,
t = initial temperature of water in calorimeter,
W_s = weight of specimen,
T_s = temperature to which the specimen is heated, and
C = mean specific heat of specimen between T_s and T.

Three separate specific heat determinations were made on each of the ceramic products and ceramic bodies. Two determinations were carried out on fourteen rock samples and all the ceramic-rock bodies; on eight rock samples, only one determination was made. For each specific heat determination a fresh specimen was used.

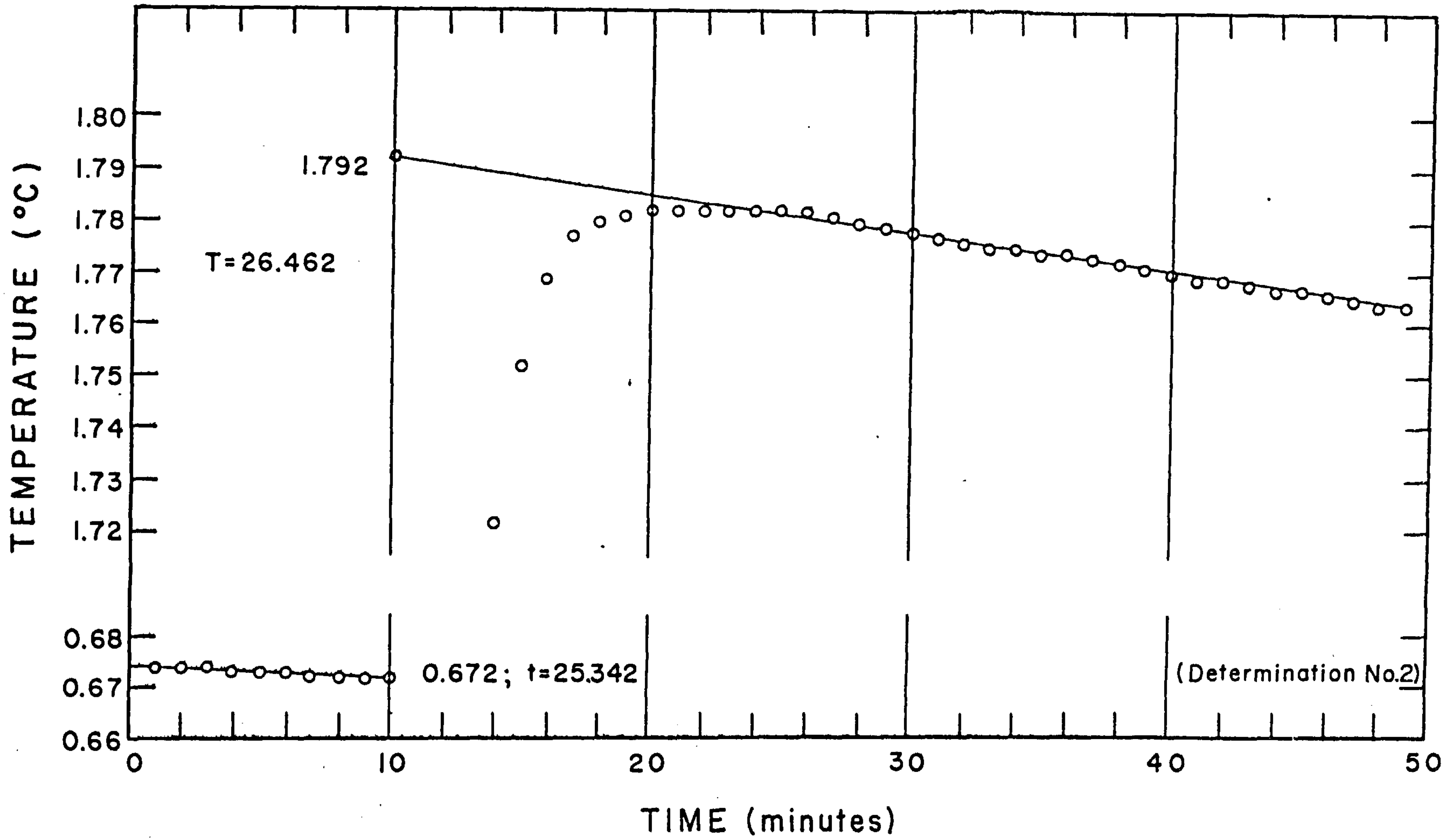

Figure 5. Time-Temperature Curve; Ceramic-Rock Body, D 3.

Accuracy of the Apparatus and of the Experimental Technique

A maximum deviation of 0.8% was established from the experimental data. Standard deviation was not calculated, because the number of runs on each material examined was limited to a maximum of three.

The precision of the results was chiefly limited by the accuracy of temperature measurements of a specimen in the furnace. Satisfactory uniformity of temperature throughout the specimen in the furnace was achieved by using a large, well insulated furnace. The large mass of the furnace was constantly maintained close to the upper temperature for the range in which the specific heats were determined. A ceramic specimen holder distributed the heat more evenly throughout the specimen. However, the fluctuation in power input caused a temperature variation of ±2°C.

The time required to transfer a specimen from the furnace to the calorimeter was small. The ceramic container with enclosed specimen was transferred by a technician wearing asbestos mittens, which prevented some heat loss. It was verified by experiment that practically all heat loss in the transferring process came from the ceramic container. The quantity of heat lost from the specimen itself was negligible.

The mass of the calorimeter was too large to be influenced by the heat radiated from the hot ceramic container during the specimen transfer interval. The distance through which the specimen fell from the container into the water of the calorimeter was about 4 inches, and as the time of fall was only a fraction of a second, the heat loss of the specimen due to convection currents and radiation was considered negligible.

The water raised by the small splash caused by the fall usually fell back into the calorimeter. The heat lost in this way, and from the few drops which occasionally escaped altogether, was extremely small. The steam produced in a fall was usually almost imperceptible.

The temperature of the water in the calorimeter was read on a Beckmann thermometer that was certified by the U. S. National Bureau of Standards. It had a range of 6.25°C and was graduated in hundredths of a degree. The readings were carried out up to ± 0.001°C and the necessary corrections were applied.

One uncertainty in measuring heat capacity was the amount of heat transferred between the calorimeter and its environment. To approach the best possible conditions, extreme care was employed in keeping the temperature of the room and the initial temperature of the calorimeter close to the same value. Because the room temperature was not automatically controlled, there was some variation from the initial temperature of the calorimeter. Normally this variation was not more than a few tenths of a degree, but if there was too great a difference the determinations of the specific heats were not carried out.

The specimens were weighed on a sensitive balance with an accuracy of ± 0.05 g.

An important factor encountered in all the specific heat calculations was the heat capacity of the calorimeter system. To determine it the copper cylinder, with or without water, was heated in a large water bath which was maintained at constant temperature. The water in the copper cylinder was weighed, and the temperatures involved in the determination of the heat capacity were measured with the same care as for the determination of the specific heats.

Bulk Density and Apparent Specific Gravity of Ceramic Products, Ceramic Bodies, and Ceramic-Rock Bodies

The bulk densities and apparent specific gravities of the ceramic products, ceramic bodies, and ceramic-rock bodies were determined in the following manner:

> A rough cube 1½ in. side was cut from each specimen that was used for the specific heat determination. Three to four test cubes were prepared from each product and body. The test pieces were dried at 110°C for about 2 hours, weighed, and placed in a glass vessel. The vessel was inserted in a vacuum desiccator and the test cubes were saturated with kerosene that was slowly introduced into the glass vessel under reduced pressure. "Saturated" and "suspended" weights of the test cubes were obtained, and the bulk densities and apparent specific gravities were calculated as prescribed in ASTM C20-46.

The apparent specific gravities were not used in calculations, but were merely determined for comparison with bulk densities.

True Density of Rocks

The true densities of the rock samples were determined in accordance with ASTM Designation C135-47. Kerosene was used as a displacement liquid, at a reduced pressure of approximately two inches of mercury.

RESULTS AND DISCUSSION

The mean specific heats, the bulk densities, the apparent specific gravities, and the heat capacities that were obtained on the selected ceramic products and on the two- and three-component ceramic bodies A and B are compiled in Tables 8, 9 and 10. The data for each mean specific heat determination are given in detail. Since the ceramic products and the ceramic bodies are more or less porous materials, their heat capacity per unit volume is given as the product of the bulk density and the mean specific heat.

From the results shown in Table 8 it can be seen that the mean specific heat and the heat capacity values of the high-alumina and the periclase brick are superior to most of the ceramic products in this table. The mean specific heat and the heat capacity of the periclase brick are higher than the mean specific heat and the heat capacity of the alumina brick. The magnesite brick has almost the same mean specific heat as the periclase brick, but its bulk density is low. Consequently, the heat capacity of the magnesite brick is only moderate. The silica, the fireclay, and the building brick have lower mean specific heats and heat capacities than have the former three ceramic products. The mean specific heat of the silica brick is somewhat higher than that of the fireclay and the building brick. However, the heat capacity of the building brick is higher than that of the silica brick and of the fireclay brick. The mean specific heat of the graphite brick is the highest of all the ceramic products examined, but its bulk density is low, and therefore its heat capacity per unit volume is lower

TABLE 8

Mean Specific Heats, Heat Capacities, Bulk Densities, and Apparent Specific Gravities of Ceramic Products (Bricks)

Bricks	No. of Runs	W_s	T_s	t	T	T-t	Mean Specific Heat between T_s and T, cal/g.°C		Bulk Density, g/cm^3	Apparent Specific Gravity	Heat Capacity Per Unit Volume between T_s and T, cal/cm^3.°C
High Alumina Brick	1	441.32	456.1	25.452	26.730	1.278	0.241	0.240	3.04	3.84	0.730
	2	444.67	456.1	25.484	26.769	1.285	0.241				
	3	447.27	456.1	25.246	26.530	1.284	0.239				
Periclase Brick	1	405.18	456.1	25.720	26.980	1.260	0.259	0.258	3.00	3.51	0.774
	2	401.87	456.1	25.346	26.592	1.246	0.258				
	3	422.80	456.1	26.389	27.699	1.310	0.258				
Magnesite Brick	1	368.90	456.1	25.539	26.674	1.135	0.256	0.256	2.54	3.11	0.650
	2	373.96	456.1	25.454	26.607	1.153	0.257				
	3	368.65	456.1	25.534	26.669	1.135	0.256				
Silica Brick	1	300.15	456.1	25.529	26.365	0.836	0.232	0.231	1.80	2.36	0.416
	2	292.60	456.1	25.416	26.230	0.814	0.231				
	3	304.56	456.1	25.480	26.325	0.845	0.231				
Graphite Brick	1	230.46	456.1	25.344	26.120	0.776	0.280	0.280	2.11	2.79	0.591
	2	235.95	456.1	25.562	26.355	0.793	0.279				
	3	230.50	456.1	25.485	26.260	0.775	0.280				
Fireclay Brick	1	254.59	456.1	25.477	26.169	0.692	0.226	0.227	1.83	2.48	0.415
	2	251.16	456.1	26.277	26.915	0.688	0.228				
	3	262.00	456.1	25.467	26.183	0.716	0.227				
Building Brick	1	299.65	456.1	25.392	26.185	0.793	0.220	0.222	2.03	2.58	0.451
	2	280.81	456.1	25.422	26.172	0.750	0.222				
	3	284.06	456.1	25.487	26.244	0.757	0.222				

TABLE 9

Mean Specific Heats, Heat Capacities, Bulk Densities, and Apparent Specific Gravities of Two-Component Ceramic Bodies

Bodies		No. of Runs	W_s	T_s	t	T	T-t	Mean Specific Heat between T_s and T, cal/g.°C		Bulk Density, g/cm^3	Apparent Specific Gravity	Heat Capacity Per Unit Volume between T_s and T, cal/cm^3.°C
Code	Compositions											
A_1	Magnesite clinker 75% Ciment Fondu 25%	1	367.85	456.0	25.472	26.631	1.159	0.262	0.262	2.42	3.40	0.634
		2	371.28	456.0	25.449	26.623	1.174	0.263				
		3	373.70	456.0	25.300	26.471	1.171	0.261				
A_2	Chrome-Magnesite 75% Ciment Fondu 25%	1	413.63	456.0	25.359	26.491	1.132	0.228	0.228	2.46	3.49	0.561
		2	399.95	456.0	25.470	26.565	1.095	0.228				
		3	414.45	456.0	25.456	26.590	1.134	0.228				
A_3	Fireclay Brick 75% Ciment Fondu 25%	1	313.37	456.0	25.357	26.216	0.859	0.228	0.229	1.78	2.69	0.408
		2	310.14	456.0	25.428	26.285	0.857	0.230				
		3	317.10	456.0	25.357	26.232	0.875	0.229				
A_4	Building Brick 75% Ciment Fondu 25%	1	281.72	456.0	25.411	26.187	0.776	0.229	0.230	1.68	2.71	0.386
		2	289.00	456.0	25.457	26.257	0.800	0.230				
		3	282.46	456.0	25.400	26.182	0.782	0.230				
A_5	Silicon Carbide 75% Ciment Fondu 25%	1	332.49	456.0	25.622	26.577	0.955	0.239	0.239	2.06	3.08	0.492
		2	357.05	456.0	25.547	26.576	1.029	0.240				
		3	328.22	456.0	25.448	26.393	0.945	0.239				

TABLE 10

Mean Specific Heats, Heat Capacities, Bulk Densities, and Apparent Specific Gravities of Three-Component Ceramic Bodies

Bodies		No. of Runs	W_s	T_s	t	T	T-t	Mean Specific Heat between T_s and T, cal/g.°C		Bulk Density, g/cm^3	Apparent Specific Gravity	Heat Capacity Per Unit Volume between T_s and T, cal/cm^3.°C
Code	Compositions											
B_1	Magnesite clinker 25%	1	363.19	456.1	25.292	26.314	1.022	0.234	0.235	2.44	3.46	0.573
	Chrome-Magnesite 50%	2	417.93	456.1	25.512	26.692	1.180	0.235				
	Ciment Fondu 25%	3	386.45	456.1	25.445	26.535	1.090	0.235				
B_2	Magnesite clinker 25%	1	329.00	456.1	25.392	26.353	0.961	0.243	0.243	2.01	2.91	0.488
	Fireclay Brick 50%	2	325.22	456.1	25.417	26.364	0.947	0.242				
	Ciment Fondu 25%	3	346.03	456.1	25.375	26.391	1.016	0.244				
B_3	Magnesite clinker 25%	1	229.61	456.1	25.441	26.123	0.682	0.247	0.246	1.89	2.95	0.465
	Building Brick 50%	2	263.20	456.1	26.196	26.969	0.773	0.245				
	Ciment Fondu 25%	3	296.43	456.1	26.372	27.247	0.875	0.246				
B_4	Magnesite clinker 50%	1	437.13	456.1	28.972	30.202	1.230	0.236	0.237	2.45	3.44	0.581
	Chrome-Magnesite 25%	2	415.82	456.1	29.324	30.505	1.181	0.238				
	Ciment Fondu 25%	3	426.67	456.1	29.059	30.263	1.204	0.237				
B_5	Magnesite clinker 50%	1	316.80	456.1	25.436	26.393	0.957	0.251	0.250	2.30	3.23	0.575
	Fireclay Brick 25%	2	350.82	456.1	25.392	26.440	1.048	0.249				
	Ciment Fondu 25%	3	311.35	456.1	25.368	26.306	0.938	0.251				
B_6	Magnesite clinker 50%	1	333.50	456.1	25.354	26.376	1.022	0.255	0.255	2.08	3.19	0.530
	Building Brick 25%	2	329.85	456.1	25.475	26.484	1.009	0.254				
	Ciment Fondu 25%	3	334.32	456.1	25.443	26.473	1.030	0.256				
B_7	Chrome-Magnesite 25%	1	351.19	456.1	25.455	26.456	1.001	0.237	0.236	1.99	2.94	0.470
	Fireclay Brick 50%	2	339.54	456.1	26.490	27.447	0.957	0.235				
	Ciment Fondu 25%	3	326.32	456.1	26.500	27.434	0.934	0.237				
B_8	Chrome-Magnesite 50%	1	349.22	456.1	25.454	26.439	0.985	0.234	0.234	2.23	3.06	0.522
	Fireclay Brick 25%	2	371.72	456.1	25.382	26.427	1.045	0.234				
	Ciment Fondu 25%	3	379.72	456.1	25.379	26.448	1.069	0.234				

than that of the magnesite brick.

The results compiled in Tables 9 and 10 indicate that the thermal properties of the ceramic bodies are inferior to those of the high-alumina brick, the periclase brick and the magnesite brick. The difference is even greater because the given specific heat values of the bodies containing Ciment Fondu are too high by about 0.008 cal/g. °C. This extra heat comes from the hydration of Ciment Fondu when the specimen is dropped in the calorimeter water. However, the values obtained were considered satisfactory for comparison.

Ceramic body A_1 in Table 9 consists of magnesite clinker and Ciment Fondu in the ratio of 3:1. It has the highest heat capacity in the two-component ceramic body group. Body A_2 is the next highest; it has low mean specific heat but adequate heat capacity. The bodies A_3 and A_4 do not have magnesite clinker in their compositions and their mean specific heat and heat capacity values are low. Replacing 75 per cent of fireclay brick or building brick with an equal portion of silicon carbide produced the results indicated for body A_5.

The results shown in Table 10 follow the same general trend as the results reported in Table 9, i.e.,the bodies with high magnesite clinker content have high mean specific heats and high heat capacities. The three-component ceramic body B_1 (consisting of magnesite clinker, crushed chrome-magnesite brick,and Ciment Fondu in the ratio of 1:2:1) has relatively high heat capacity. If the magnesia in the chrome-magnesite brick is taken into consideration, the body B_1 has a high magnesia content of about 40 per cent. In addition, the bulk density of the chrome-magnesite brick is high. Replacing 50 per cent of chrome-magnesite brick with an equal quantity of fireclay brick or building brick, thus reducing the magnesia content from about 40 per cent to about 25 per cent, produced results as indicated for B_2 and B_3. These two bodies have slightly higher mean specific heats than B_1, but their bulk densities are low and the heat capacities are inferior to B_1. Three-component ceramic bodies with a heat capacity similar to that of B_1 can be prepared, if magnesite clinker and Ciment Fondu are used with chrome-magnesite, fireclay, or building brick in the ratio of 2:1:1. Bodies B_4, B_5 and B_6 are typical of such compositions. An increase in the magnesite clinker content improves the specific heat and the heat capacity values. Further, the chrome-magnesite can be successfully replaced by less expensive fillers, such as fireclay and building brick. Compositions consisting of chrome-magnesite, fireclay brick, and Ciment Fondu in the ratios of 1:2:1 and 2:1:1 produced results indicated for B_7 and B_8. The specific heat values of B_7 and B_8 are lower,but the heat capacities are slightly higher than those of the bodies B_2 and B_3.

The mean specific heats, the true densities,and the heat capacities,which were obtained on the rock samples,are compiled in Tables 11 and 12. The data of each mean specific heat determination are given in detail. Because the results of the seventeen rock.samples, as shown in Table 11, were also used for another project,their mean specific heats were determined over the range of 26.0^{o} to 625^{o}C. This procedure was considered satisfactory for the requirements of this investigation. The mean specific heats of five carbonate rock samples shown in Table 12 were determined over the range of 26.0^{o} to 456^{o}C. Since the porosities of most of the rocks examined are low, their heat capacity per unit volume is given as the product of the true density and the mean specific heat.

TABLE 11

Mean Specific Heats, Heat Capacities, and True Densities of Rocks

Sample		No. of Runs	W_s	T_s	t	T	T-t	Mean Specific Heat between T_s and T, cal/g.°C		True Density, g/cm^3	Heat Capacity Per Unit Volume between T_s and T, cal/cm^3.°C
Rocks	No.										
Aloite Granite	M-195	1	438.30	625.0	25.007	26.774	1.767	0.241	0.241	2.650	0.639
		2	464.60	625.0	25.586	27.453	1.867	0.240			
Anorthosite	M-193	1	474.54	625.0	25.595	27.457	1.862	0.235	0.234	2.825	0.661
		2	421.06	625.0	25.546	27.189	1.643	0.233			
Sandstone	M-176	1	344.47	625.0	25.411	26.826	1.415	0.245	0.246	2.657	0.654
		2	345.40	625.0	25.411	26.831	1.420	0.246			
Gabbro	M-178	1	441.96	625.0	25.407	27.078	1.671	0.226	0.227	2.978	0.676
		2	439.89	625.0	25.387	27.064	1.677	0.228			
Nepheline Syenite	M-188	1	367.90	625.0	25.397	26.859	1.462	0.237	0.237	2.632	0.624
		2	376.50	625.0	25.453	26.948	1.495	0.237			
Basalt	M-189	1	473.02	625.0	25.445	27.304	1.859	0.235	0.236	3.043	0.718
		2	501.72	625.0	25.532	27.517	1.985	0.237			
Rhyolite	M-190	1	367.50	625.0	25.418	26.878	1.460	0.237	0.237	2.664	0.631
		2	321.31	625.0	25.340	26.617	1.277	0.237			
Syenite	M-191	1	432.46	625.0	25.452	27.116	1.664	0.230	0.229	2.637	0.604
		2	447.81	625.0	25.526	27.237	1.711	0.228			
Nordmarkite	M-192	1	419.50	625.0	25.351	26.968	1.617	0.230	0.231	2.660	0.614
		2	418.10	625.0	25.500	27.123	1.623	0.232			
"Graywacke"	M-199	1	427.90	625.0	25.423	27.078	1.655	0.231		3.073	0.710
"Iron Formation"	M-200	1	551.32	625.0	25.414	27.320	2.106	0.227		3.300	0.749
Granite	M-194	1	392.21	625.0	25.413	26.975	1.563	0.238		2.649	0.630
Granodiorite	M-208	1	358.40	625.0	25.435	26.859	1.424	0.237		2.766	0.656
Granite	M-209	1	468.91	625.0	25.358	27.213	1.855	0.237		2.660	0.630
Quartz Monzonite	M-210	1	381.65	625.0	25.275	26.808	1.533	0.240		2.676	0.642
"Quartz Rock"	M-179	1	277.25	625.0	25.327	26.487	1.160	0.250		2.660	0.665
Quartzite	M-207	1	356.79	625.0	25.323	26.810	1.487	0.249		2.665	0.664

TABLE 12

Mean Specific Heats, Heat Capacities, and True Densities of Carbonate Rocks

Sample		No. of Runs	W_s	T_s	t	T	T-t	Mean Specific Heat between T_s and T, cal/g.°C		True Density, g/cm^3	Heat Capacity Per Unit Volume between T_s and T, cal/cm^3.°C
Rocks	No.										
Limestone	M-184	1	377.41	456.0	25.493	26.592	1.100	0.242			
		2	387.79	456.0	25.453	26.574	1.116	0.239	0.241	2.728	0.657
Limestone (Recrystallized)	M-185	1	459.87	456.0	25.519	26.853	1.334	0.242			
		2	421.35	456.0	25.513	26.721	1.208	0.240	0.241	2.740	0.660
Magnesian Limestone	M-187	1	442.81	456.0	25.409	26.696	1.287	0.242			
		2	399.85	456.0	25.446	26.613	1.167	0.243	0.243	2.752	0.669
Dolostone	M-186	1	312.00	456.0	25.469	26.414	0.945	0.252			
		2	392.00	456.0	25.009	27.183	1.174	0.250	0.251	2.500	0.628
Dolostone	M-168	1	477.00	456.0	24.922	26.378	1.456	0.253			
		2	450.32	456.0	25.445	26.815	1.370	0.253	0.253	2.856	0.722

TABLE 13

Mean Specific Heats, Heat Capacities, Bulk Densities, and Apparent Specific Gravities of Two-Component Ceramic-Rock Bodies

Bodies		No. of Runs	W_s	T_s	t	T	T-t	Mean Specific Heat between T_s and T, cal/g.°C		Bulk Density, g/cm^3	Apparent Specific Gravity	Heat Capacity Per Unit Volume between T_s and T, cal/cm^3.°C
Code	Compositions											
C_1	"Quartz-Rock," M-179 75%	1	286.24	456.0	25.509	26.302	0.793	0.245				
	Ciment Fondu 25%	2	312.65	456.0	25.387	26.251	0.864	0.244	0.245	2.03	2.75	0.497
C_2	Quartzite, M-207 75%	1	325.50	456.0	25.432	26.333	0.901	0.245				
	Ciment Fondu 25%	2	280.60	456.0	25.385	26.165	0.780	0.246	0.246	1.99	2.69	0.490
C_3	Sandstone, M-176 75%	1	312.10	456.0	25.563	26.424	0.861	0.244				
	Ciment Fondu 25%	2	315.05	456.0	25.419	26.295	0.876	0.246	0.245	1.99	2.76	0.488
C_4	Granite, M-195 75%	1	311.60	456.0	25.622	26.489	0.867	0.246				
	Ciment Fondu 25%	2	306.30	456.0	25.442	26.288	0.846	0.244	0.245	1.99	2.77	0.488
C_5	Magnesian Limestone, M-187 75%	1	321.90	456.0	25.425	26.362	0.937	0.257				
	Ciment Fondu 25%	2	312.95	456.0	25.389	26.297	0.908	0.257	0.257	2.05	2.78	0.527
C_6	Dolostone, M-186 75%	1	280.69	456.0	25.422	26.241	0.819	0.258				
	Ciment Fondu 25%	2	335.20	456.0	25.395	26.379	0.984	0.259	0.259	2.03	2.90	0.526
C_7	Dolostone, M-168 75%	1	333.90	456.0	25.481	26.458	0.977	0.259				
	Ciment Fondu 25%	2	332.48	456.0	25.436	26.417	0.981	0.261	0.260	2.12	2.86	0.551

The thermal properties of the seventeen rocks, as listed in Table 11, are inferior to those obtained on the high alumina brick and the periclase brick. As the specific heat of the materials used here decreases with decreasing temperature, the thermal properties of these rocks could be expected to be even lower if the rocks were examined between 26.0° and 456°C. Granite M-195, Sandstone M-176, "Quartz Rock" M-179, and Quartzite M-207 have high specific heats and moderate heat capacities and are abundant in nature; because of this they were selected as constituents for ceramic-rock bodies. Basalt M-189, "Graywacke" M-199, and "Iron Formation" M-200 have higher heat capacities than those of the former four rocks, but they are less common and non-homogeneous. The thermal properties of the other non-carbonate rocks are lower, and could be compared with the thermal properties of the bodies A_1 and A_2 in Table 9 and of the bodies B_1, B_4, and B_5 in Table 10.

The thermal properties of the five carbonate rocks in Table 12 appear to be similar to those of the best rocks in Table 11. It will be noted that the results on carbonate rocks were obtained at a lower temperature interval. If this is taken into consideration, then the thermal properties of carbonate rocks are superior. Dolostone M-168 has thermal properties that are very close to the specific heat and the heat capacity of the magnesite brick in Table 8. Because such rocks are abundant in nature, Magnesian Limestone M-187, Dolostone M-186, and Dolostone M-168 were selected as constituents for ceramic-rock bodies. The carbonate rocks have a deficiency as thermal storage media, because decomposition may take place when such materials are heated. This may happen in the vicinity of electrical heating elements where the decomposition temperature of the carbonate rocks could be reached. The calcined part may hydrate on cooling by picking up air moisture and thus cause the disintegration of the body. This shortcoming could be avoided if stabilized materials such as dead-burned magnesia or stabilized dolostone were used.

The results obtained on the two-, the three-, and the four-component ceramic-rock bodies are given in Tables 13, 14 and 15. Here, again, the given mean specific heat values of the bodies containing Ciment Fondu are too high by about 0.008 cal/g.°C. As the same amount of high-alumina cement was used for all the ceramic-rock compositions, the results were considered satisfactory for comparison.

The thermal properties of seven two-component ceramic-rock bodies, shown in Table 13 and designated from C_1 to C_7, have higher mean specific heats but lower heat capacities than pure rock samples. Bodies C_5, C_6 and C_7, containing some magnesian compounds, have higher thermal properties than C_1, C_2, C_3 and C_4, which do not contain magnesian compounds. By comparing the thermal properties of bodies A_3 and A_4 in Table 9 with those of bodies C in Table 13, it can be seen that the thermal properties of the latter are superior. This indicates that, in two-component bodies consisting of filler and Ciment Fondu in the ratio of 3:1, the seven rocks listed in Table 13 are just as effective or even better as fillers than the fireclay brick and the building brick.

The results shown in Table 14 prove again that the bodies with high magnesite clinker content have high mean specific heats and high heat capacities. The three-component body D_1, consisting of magnesite clinker, quartzite, and Ciment Fondu in the ratio of 2:1:1, has high mean specific heat and relatively high heat capacity.

TABLE 14

Mean Specific Heats, Heat Capacities, Bulk Densities, and Apparent Specific Gravities of Three-Component Ceramic-Rock Bodies

Bodies		No. of Runs	W_s	T_s	t	T	T-t	Mean Specific Heat between T_s and T, cal/g.°C		Bulk Density, g/cm³	Apparent Specific Gravity	Heat Capacity Per Unit Volume between T_s and T, cal/cm³.°C
Code	Compositions											
D_1	Magnesite clinker 50% Quartzite, M-207 25% Ciment Fondu 25%	1	372.17	456.0	25.460	26.545	1.085	0.258				
		2	364.83	456.0	25.515	25.580	1.065	0.258	0.258	2.24	3.01	0.578
D_2	Magnesite clinker 25% Quartzite, M-207 50% Ciment Fondu 25%	1	334.80	456.0	25.507	26.471	0.964	0.255				
		2	354.60	456.0	25.460	26.483	1.023	0.255	0.255	2.08	2.83	0.530
D_3	Magnesite clinker 50% Sandstone, M-176 25% Ciment Fondu 25%	1	382.10	456.0	25.430	26.534	1.104	0.257				
		2	386.63	456.0	25.342	26.462	1.102	0.256	0.257	2.28	3.06	0.586
D_4	Magnesite clinker 25% Sandstone, M-176 50% Ciment Fondu 25%	1	362.90	456.0	25.429	26.459	1.030	0.251				
		2	341.70	456.0	25.496	26.474	0.978	0.253	0.252	2.14	2.92	0.539
D_5	Magnesite clinker 50% Granite, M-195 25% Ciment Fondu 25%	1	362.58	456.0	25.442	26.501	1.059	0.258				
		2	350.77	456.0	25.328	26.346	1.018	0.257	0.258	2.31	3.11	0.596
D_6	Magnesite clinker 25% Granite, M-195 50% Ciment Fondu 25%	1	329.86	456.0	25.491	26.416	0.925	0.248				
		2	351.95	456.0	25.397	26.385	0.988	0.248	0.248	2.15	2.89	0.533

TABLE 15

Mean Specific Heats, Heat Capacities, Bulk Densities, and Apparent Specific Gravities of Four-Component Ceramic-Rock Bodies

Bodies		No. of Runs	W_s	T_s	t	T	T-t	Mean Specific Heat between T_s and T, cal/g.°C		Bulk Density, g/cm³	Apparent Specific Gravity	Heat Capacity Per Unit Volume between T_s and T, cal/cm³.°C
Code	Compositions											
E_1	Magnesite clinker 25% Sandstone, M-176 25% Magnesian Limestone, M-187 25% Ciment Fondu 25%	1	314.95	456.0	25.436	26.333	0.897	0.252				
		2	353.77	456.0	25.466	26.433	1.017	0.254	0.253	2.16	2.86	0.546
E_2	Magnesite clinker 25% Granite, M-195 25% Magnesian Limestone, M-187 25% Ciment Fondu 25%	1	354.10	456.0	25.489	26.493	1.004	0.251				
		2	373.54	456.0	25.485	26.552	1.067	0.253	0.252	2.17	2.90	0.547

Replacing 25 per cent of magnesite clinker with an equal quantity of quartzite produced results as indicated for D_2. The mean specific heat of D_2, was only slightly affected, but the bulk density was lowered considerably and therefore the heat capacity is lower. The same applies to D_3, D_4, D_5, and D_6. Generally, the three-component ceramic-rock bodies D have better thermal properties than C_1, C_2, C_3, and C_4 in Table 13. By comparing the thermal properties of bodies B_2 and B_3 in Table 10 with those of D_2, D_4, and D_6, it can be seen that the thermal properties of the latter three are superior. This indicates that in the three-component bodies consisting of magnesite clinker, fireclay brick (or building brick), and Ciment Fondu in the ratio of 1:2:1, the fireclay brick (or building brick) might be successfully replaced by quartzite, sandstone, or granite.

The bodies D_4 and D_6 were modified to form two four-component bodies E_1 and E_2, as shown in Table 15. In an attempt to improve the thermal properties, 25 per cent of sandstone in E_1 and 25 per cent of granite in E_2 were replaced by an equal amount of magnesian limestone. The results of tests indicate that E_1 and E_2 do not have improved thermal properties. Their mean specific heats and heat capacities remain very close to those of D_4 and D_6. Obviously, the magnesian limestone was not a material that could profitably replace the sandstone or the granite. Possibly the Dolostone M-168 might be a better material to serve this purpose.

CONCLUSIONS

By means of a calorimeter, using water, it has been established that the samples of ceramic products, ceramic bodies, selected carbonate rocks, and ceramic-rock bodies have mean specific heat values ranging from 0.222 to 0.262 cal/g.°C, and heat capacities per unit volume ranging from 0.386 to 0.774 $cal/cm^3.^\circ C$, over the range of 26.0° and 456°C. It was also established that the seventeen selected rock samples have mean specific heats from 0.227 to 0.250 cal/g.°C, and heat capacities per unit volume ranging from 0.604 to 0.749 $cal/cm^3.^\circ C$, over the range of 26.0° and 625°C.

The thermal properties of the materials and the bodies investigated are as follows:

1. 'Highly calcined' alumina (over 99% Al_2O_3) and dead-burned magnesia (over 93% MgO) have high mean specific heat values. Having high bulk densities, both materials have also high heat capacities.

2. The silica brick, the fireclay brick, and the building brick have lower mean specific heats and heat capacities than the calcined alumina and dead-burned magnesia. The mean specific heat of silica brick is higher than that of the fireclay brick and the building brick. However, the heat capacity of the building brick is higher than that of the silica brick and of the fireclay brick.

3. The mean specific heat of the graphite brick is the highest of all the ceramic products examined. However, its bulk density is low, and hence the heat capacity of the graphite brick is lower than that of the magnesite brick.

4. The thermal properties of the two- and the three-component ceramic bodies are inferior to those of 'highly

calcined' alumina and dead-burned magnesia. Magnesite clinker with Ciment Fondu, in the ratio of 3:1, has the highest mean specific heat and the highest heat capacity in the two-component ceramic body group. The mean specific heats and the heat capacities of the two-component bodies are lowered when the magnesite clinker is replaced by chrome-magnesite, fireclay brick, or building brick.

Three-component ceramic bodies follow the same trend: the bodies with high magnesite clinker content have high mean specific heats and high heat capacities. Any attempt to reduce the magnesite clinker content in the three-component bodies lowers the values of these properties.

5. The mean specific heats and the heat capacities of seventeen rocks investigated are lower than those of calcined pure alumina and dead-burned magnesia. Common rocks such as granite, sandstone, quartzite,and "quartz-rock" have relatively high mean specific heats and moderate heat capacities. They can successfully replace fireclay brick and building brick in some body compositions.

The five carbonate rocks investigated showed thermal properties superior to those of granite, sandstone, quartzite, and "quartz-rock". The mean specific heat and the heat capacity of dolostone are very close to the specific heat and the heat capacity of the magnesite brick. Stabilized dolostone might be considered as an effective substitute for dead-burned magnesia.

6. The two-, three-,and four-component ceramic-rock

bodies have higher mean specific heats but lower heat capacities than have the pure rock samples. Two-component ceramic-rock bodies containing some magnesian compounds have higher mean specific heats and heat capacities than have those that do not contain magnesian compounds; similarly, three- and four-component ceramic-rock bodies with high magnesite clinker content have high mean specific heats and high heat capacities. Any attempt to reduce the magnesite clinker content in the three- and four-component ceramic-rock bodies lowers the values of these thermal properties.

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The investigation has provided evidence that 'highly calcined' pure alumina and dead-burned magnesia have the best specific heats and heat capacities of the ceramic products and rocks examined. Two-, three-,and four-component bodies from ceramic products or ceramic products and rocks bonded with Ciment Fondu, are economically more attractive but have lower heat capacities than have calcined alumina and dead-burned magnesia, bonded with the same bond.

Within the scope of this work,it is concluded that materials and material compositions rich in dead-burned magnesia are excellent thermal storage media costing less than other materials and material compositions having similar heat capacities. Reduction of magnesia content in the ceramic and rock bodies lowers their mean specific heats and heat capacities and, consequently, their value as thermal storage media.

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