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NON-METALLIC THERMAL STORAGE MEDIA FOR BLOCK-TYPE ELECTRIC SPACE HEATERS

V.D. SVIKIS

MINERAL PROCESSING DIVISION

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NON-METALLIC THERMAL STORAGE MEDIA FOR BLOCK-TYPE ELECTRIC SPACE HEATERS

by

V. D. Svikis *

ABSTRACT

A series of low-cost non-metallics was submitted to determinations of thermal properties, such as mean specific heat and heat capacity per unit volume, to evaluate their suitability as thermal-storage media for block-type electric space heaters. For this work a special electric furnace and a large calorimeter using water were designed and constructed.

The mean specific-heat determinations were made by the method of mixtures. The heat capacities per unit volume were calculated from the densities and mean specific heats of the materials examined.

The results indicate that of the ceramic products, rocks and mineral concentrates examined, dead-burned magnesia (over 95% MgO), 'highly calcined' alumina (over 99% Al_2O_3), hematite concentrate, and rocks rich in hematite, magnetite and/or magnesian compounds have high heat capacities. Two- and three-component bodies from ceramic products or ceramic products and rocks, bonded with aluminous cement, are economically more attractive but their heat capacities are lower than those of their single components without the cement bond. In certain cases, the dead-burned magnesia and the calcined alumina -- relatively expensive materials -- can be successfully replaced in these body compositions by mineral concentrates and rocks, such as hematite concentrate, magnetite ore, olivine, and talc. The fireclay brick and the building brick can be successfully substituted by common rocks, such as sandstone, quartzite and granite.

It is concluded that materials and material compositions rich in hematite, magnetite, and magnesian compounds are excellent low-cost thermal-storage media for block-type electric space heaters.

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Direction des mines

Rapport de recherches R 206

MATÉRIAUX NON MÉTALLIQUES POUR RADIATEURS ÉLÉCTRIQUES À ACCUMULATION

par

V. D. Svikis*

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RÉSUMÉ

Divers matériaux non métalliques peu dispendieux ont été soumis à des essais de détermination de leurs propriétés thermiques telles que la chaleur spécifique moyenne et la capacité thermique par unité de volume, afin d'estimer la possibilité de leur usage comme accumulateurs de chaleur dans les radiateurs électriques du type "bloc". À cette fin un four électrique spécial et un grand calorimètre ont été conçus et construits.

Les mesures de la chaleur spécifique moyenne ont été effectuées par la méthode des mélanges. Les capacités thermiques des matériaux examinés ont été déterminées à partir des densités et des chaleurs spécifiques moyennes.

Les résultats montrent que parmi les produits céramiques, les roches et les concentrés des minéraux examinés, la magnésie grillée à mort (plus de 95% de MgO), l'alumine calcinée à fond (plus de 99% de Al_2O_3), les concentrés d'hématite et les roches à forte teneur en hématite, en magnétite ou en composés magnésiens, présentent les meilleures capacités thermiques. Les composés à deux ou trois éléments des produits céramiques ou des mélanges de produits céramiques et de roches, liés par un ciment alumineux, sont plus attrayants économiquement, mais leurs capacités thermiques sont inférieures à ceux de leurs éléments constitutifs sans liant. En certains cas la magnésie grillée à mort et l'alumine calcinée, des matériaux assez coûteux, peuvent être remplacés avec succès dans ces mélanges par des concentrés de minéraux et des roches, comme par exemple par un concentré d'hématite, de magnétite, d'olivine ou de talc. Il est possible de remplacer avec succès la brique réfractaire et la brique de construction par des roches ordinaires comme le grès, le quartzite ou le granit.

En conclusion, les matériaux ou les composés riches en hématite ou en magnétite, ainsi que les composés magnésiens, sont d'excellentes substances à bon marché pour l'accumulation de chaleur, pouvant être utilisés dans les radiateurs électriques à accumulation.

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INTRODUCTION

Recent technological advances and developments within the electric power generating industry have made the cost of electrical energy competitive with other heating media in many industrial fields as well as in space heating. The cost of electricity would be at a minimum if consumers could take supplies of electric power during the night at off-peak hours.[1,2] The use of off-peak electrical energy for heating is a logical development in power-station economy. This problem will be especially important when nuclear-power stations begin to produce electric power. An adequate off-peak load will have to be ensured; otherwise, the electric power available at the time of light load will have to be turned to waste, resulting in loss of efficiency and in increased costs.

Electrical energy, as supplied to the public, is different from fuels in that it cannot be stored unless it is converted into some form of thermal energy. Consequently, an off-peak electrical heating system must make use of a medium that can store thermal energy. In earlier thermal-storage heating systems, soapstone and cast iron were used as thermal-storage media; later, they were replaced by fire brick and building brick. Modern block-type space heaters are filled with refractories or blocks made of refractory concrete. When such blocks are heated by properly designed electrical heating elements to about 430°C, they store electrically generated heat. The blocks, or batteries of blocks, can be economically heated at night by utilizing low rate off-peak electrical energy. During the day, when both industry and households require a large amount of electric power, the block-type thermal storage 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-type heaters have been quite popular in Europe. At present they are also gaining popularity in Canada and in the United States.

SCOPE OF INVESTIGATION

This work was undertaken to develop non-metallic thermal-storage media that can be used in block-type electric space heaters. Their principal requirements are high heat capacity and economic production costs. Accordingly, some ceramic products, rocks, and similar materials of low cost were selected and examined to determine whether they meet these requirements.

A well-insulated muffle furnace and a large-capacity calorimeter using water were designed and constructed for this investigation.

The mean specific heats and the densities of the selected materials and their compositions were determined. 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 work has been devoted to ceramic materials and products, particularly to refractories. However, fewer data are available on the specific heats of rocks and minerals.

The specific heats of fireclay bricks have been studied over a wide range of temperature and reported by several investigators, among them Wilson, Holdcroft and Mellor,[3] Bradshaw and Emery,[4] Heyn, Bauer and Wetzel,[5] Todokoro,[6] and MacGee.[7]

Commercial magnesite and magnesite bricks have been studied and reported by Heyn et al.,[5] Todokoro,[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 chrome ores and reported specific heats between 25° and 850°C. Specific heats of chrome ores and chrome bricks have also been determined by Todokoro.[6]

The specific heats on silica bricks have been studied by Todokoro,[6] Heyn et al.,[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, insulating 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. Determinations of the specific heats of some refractory materials have been reported by Clements.[18]

Few references on the specific heats of minerals and rocks are found in the literature. Todokoro[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.

The literature survey 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 the various authors.

In view of the above literature survey, and of the specific requirements of this work, it was realized that the specific heats of the selected ceramic products and rocks, and particularly of their body compositions, should be investigated.

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.

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:

(1)	High-alumina brick	(99.4% Al_2O_3)
(2)	Periclase brick	(93.0% MgO)
(3)	Magnesite brick	(85.0% MgO)
(4)	Silica brick	(94.5% SiO_2)
(5)	Fireclay brick	(37.0% Al_2O_3, 60.0% SiO_2)
(6)	Building brick	(16.0% Al_2O_3, 56.0% SiO_2)
(7)	Dead-burned magnesia (magnesite clinker)	(95.4% MgO)
(8)	Chrome-magnesite brick (crushed)	(70.0% Cr_2O_3, 30.0% MgO)
(9)	Aluminous-cement clinker	(approx. 40.0% Al_2O_3)
(10)	Aluminous cement	(approx. 40.0% Al_2O_3)

Ceramic products from (1) to (4) were investigated principally as single materials. They were considered as the basis for comparison. Products from (5) to (9) were employed as constituents in ceramic bodies. Aluminous cement was used chiefly as a binder in body compositions; however, it was considered as one of the body constituents in all bodies made from ceramic products and rocks.

Ceramic Body Compositions

The ceramic bodies consisted of two and three ceramic components. Identifications and compositions of the ceramic bodies are given in Tables 1 and 2.

TABLE 1

Compositions of Bodies with Two Ceramic Components

Bodies	Magnesite Clinker, %	Chrome-Magnesite Brick, %	Fireclay Brick, %	Building Brick, %	Aluminous Cement Clinker, %	Aluminous Cement, %
A1	75	-	-	-	-	25
A2	-	75	-	-	-	25
A3	-	-	75	-	-	25
A4	-	-	-	75	-	25
A5	-	-	-	-	75	25

TABLE 2

Compositions of Bodies with Three Ceramic Components

Bodies	Magnesite Clinker, %	Chrome-Magnesite Brick, %	Fireclay Brick, %	Building Brick, %	Aluminous Cement, %
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

Rocks

Thirty-four Canadian rock types and two mineral concentrates were selected for the investigation. A study of the rocks was made in the laboratories of the Mines Branch,[19] and a brief description of their mineral compositions and texture is included in Table 3.

Some of the rocks were investigated as single materials, but the majority of them, including the two mineral concentrates, were 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.

Ceramic-Rock Body Compositions

The ceramic-rock bodies consisted of two and three ceramic and rock components. Identifications of these bodies and their respective compositions are shown in Tables 4 and 5.

EXPERIMENTAL APPARATUS AND PROCEDURE

Details of the procedure, as well as of the design and operation of the equipment used in this work, have been published elsewhere.[20] Consequently, only a brief description of them will be given here. Some changes in the procedure, particularly in the specimen preparation, were made at a later stage of this work; these changes will be described in detail.

TABLE 3

Classifications and Compositions of Selected Rocks and Mineral Concentrates*

SAMPLE		CONSTITUENTS, %		TEXTURE
No.	Rocks and Mineral Concentrates	Major	Minor	
1	Albite Granite, M-195	Plagioclase, 45; Quartz, 29; K-Feldspar, 21	Biotite, 3; Muscovite, 2	Medium-grained
2	Anorthosite, M-193	Plagioclase (An_{50}), 97	K-Feldspar, 1; Augite, 1; Magnetite, 1	Coarse-grained
3	Sandstone, M-176	Quartz, 92; K-Feldspar, 8	- -	Sugary, fine-grained
4	Gabbro (Diabasic), M-178	Plagioclase (An_{50}), 46; Augite, 24; Quartz, K-Feldspar intergrowth, 12; Magnetite, 7	Hornblende, Biotite, Chlorite, 11	Diabasic, medium-grained
5	Nepheline Syenite, M-188	Plagioclase, 52; K-Feldspar, 23; Nepheline, 23	Magnetite, 1.5; Muscovite, 1	Medium-grained
6	Basalt, M-189	Epidote, 42; Quartz + Feldspar, 23; Augite, 20; Chlorite, 10	Magnetite, 5	Fine-grained, altered
7	Rhyolite, M-190	K-Feldspar, 52; Plagioclase (An_{10}), 21; Quartz, 23	Magnetite, 3; Biotite, 1	Medium-grained
8	Syenite, M-191	K-Feldspar, 69; Albite, 17; Hornblende, 9	Magnetite, 3; Biotite, 2	Medium-grained
9	Nordmarkite, M-192	Microperthite (K, Na-Feldspar intergrowth), 73; Quartz, 9; Plagioclase, 8; Hornblende, 7	Augite, 2; Magnetite + Hematite, 1	Coarse-grained
10	Granite, M-194	Quartz, 34; K-Feldspar, 31; Plagioclase, 31	Biotite, 3; Magnetite + Chlorite, 1	Medium-grained
11	Granodiorite, M-208	Plagioclase (An_{30}), 51; Quartz, 21; Hornblende, 12; Biotite, 9	K-Feldspar, 4; Epidote, 2; Sphene, 1	Medium-grained
12	Granite, M-209	Quartz, 33; K-Feldspar, 29; Plagioclase, 23; Biotite, 10	Quartz-Plagioclase, 3; Sphene, 1; Other minor constituents, 1	Medium-grained
13	Quartz Monzonite, M-210	Plagioclase (An_{28}), 42; Quartz, 27; K-Feldspar, 20; Biotite, 10	Muscovite, 1	Coarse-grained
14	"Quartz Rock", M-179	Quartz, 100	-	Coarse crystals
15	Quartzite, M-207	Quartz, 93	Muscovite, 7	Strained, fine-grained
16	Limestone, M-184	Calcite, 94	Dolomite, 4; Clay, 2	Sedimentary, fine-grained
17	Limestone, M-185	Calcite, 88; Dolomite, 10	Diopside, Quartz, Graphite, 2	Recrystallized, coarse-grained
18	Magnesian Limestone, M-187	Calcite, 72; Dolomite, 27	Impurities, 1	Fine-grained

(Continued)

TABLE 3 (cont'd)

Classifications and Compositions of Selected Rocks and Mineral Concentrates*

SAMPLE		CONSTITUENTS, %		TEXTURE
No.	Rocks and Mineral Concentrates	Major	Minor	
19	Dolostone, M-186	Dolomite, 80; Voids, 19	Sulphides, 1	Medium-grained
20	Dolostone, M-168	Dolomite, 98	Tremolite, 2	Coarse crystals
21	Microsyenite	Albite, 50; Pyroxene, 15; K-Feldspar, 10; Magnetite, 10; Biotite, 6	Hornblende, 5; Chlorite,<1.5; Quartz,<1; Apatite,<1, Pyrite,<1	Fine-grained
22	Olivine	Olivine (probably forsterite),<90	Orthopyroxene,<5; Amphibole,<5; Magnetite, Chromite, Serpentine, etc.,<1	Cataclastic
23	Dumortierite (**)	In the approximate order of abundance the constituents are: Pyrophyllite; Dumortierite; Quartz; Kaolin	Diaspore	Fine-grained
24	"Talc", dark	Chlorite,<95	Talc,<5; Rutile, trace	Fine-grained
25	Talc, dark-grey	Talc,<90; Chlorite,<10	Mica, trace	Fine-grained
26	Talc, light-grey	Talc,<90	Chlorite,<5; Mica,<5; Amphibole, trace	Fine-grained
27	Serpentine, dark-green	Serpentine (probably chrysotile), 80; Olivine,<10; Spinel,<10	Brucite (as fine-grained aggregates),<3	Medium-grained
28	Serpentine, light-green	Chrysotile, 60; Olivine, 20; Dolomite + Magnesite, 20	Brucite, trace	Medium-grained
29	Amphibole #420	Amphibole, 50; Magnetite, 40; Pyrite, 10		Medium-grained
30	Specular Hematite, Ontario	Hematite, 85; Quartz,<15	Minor constituents (unidentified), <5	Fine-grained
31	"Iron Formation"	Quartz, 75; Magnetite (plus hematite),<25	Calcite (plus minor constituents), <5	Fine-grained
32	Amphibolite	Hornblende + Chlorite, 55; Feldspar, 35	Quartz, 5; Opaque Minerals (probably magnetite), 5	Medium-grained
33	Specular Hematite, Labrador	Quartz, 55; Hematite, 45		Powder (as received)
34	Hematite Concentrate, Labrador	Hematite, 92.4; Quartz, 6.4	Minor constituents (unidentified), 1.2	Powder (as received)
35	Hematite Super-concentrate	Hematite, 99.8	Quartz, 0.2	Powder (as received)
36	Magnetite Ore, CM-323	Magnetite, 80; Pyroxene,<20	Pyrite, 1; Hematite, trace	Fine-grained

* Nos. 1-20, after J. A. Soles[19].

No. 21, after J. A. Soles, Mineralogical Report, Nov., 1963, Mineral Processing Div. Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Nos. 22-33 and 36, after R. M. Buchanan, Mineralogical Reports, Jan. and May, 1966, Mineral Processing Div., Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Nos. 34 and 35 calculated from chemical analyses, L. McCorriston and D. T. Charette, Internal Reports MS-AC-66-84 and 563, Mineral Sciences Div., Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

** The rock is too variable to provide reliable estimates of composition.

TABLE 4

Bodies with One Rock and One Ceramic Component

(Body compositions: 75% rock + 25% aluminous cement)

Bodies	Body Rock Components	Bodies	Body Rock Components
C_1	Quartzite, M-207	C_{12}	Talc, light-grey
C_2	Sandstone, M-176	C_{13}	Serpentine, dark-green
C_3	Granite, M-195	C_{14}	Serpentine, light-green
C_4	Anorthosite, M-193	C_{15}	Amphibole, #420
C_5	Gabbro, M-178	C_{16}	Specular hematite, Ontario
C_6	Basalt, M-189	C_{17}	"Iron Formation"
C_7	Microsyenite	C_{18}	Amphibolite
C_8	Olivine	C_{19}	Specular hematite, Labrador
C_9	Dumortierite	C_{20}	Hematite concentrate, Labrador
C_{10}	"Talc", dark	C_{21}	Hematite super-concentrate
C_{11}	"Talc", dark-grey	C_{22}	Magnetite ore, CM-323

TABLE 5

Compositions of Bodies with One Rock and Two Ceramic Components

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

Preparation of Test Specimens

(i) From Ceramic Products and Rocks

Commercial ceramic products, with the exception of Nos. 7 to 10, were received in the form of a brick. The rock samples had irregular sizes and shapes. One rock sample and two samples of rock concentrates were received in ground condition. Three specimens, measuring 1 1/2 in. x 1 1/2 in. x 4 in., were cut from each brick and solid rock sample. At first a hole was drilled along the 4-in. axis to the centre of each specimen, in which a thermocouple was inserted to measure the temperature of the specimen during heating; later, the temperature was measured outside the specimen and no hole was necessary.

(ii) From Ceramic Bodies and Ceramic-Rock Bodies

Ceramic products and rocks, which were selected as aggregates for bodies, were crushed, screened and graded as follows:

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

The bodies were prepared by mixing, in various proportions, graded aggregates and high-alumina cement. The identifications and compositions of the bodies are shown in Tables 1, 2, 4 and 5.

The dry-blended batch materials were tempered with the minimum amount of water. Three to four test specimens from each ceramic and ceramic-rock body were formed by tamping the mixture into 1 1/2-in. x 1 1/2-in. x 4-in. wooden moulds that were subsequently vibrated. After 24-hour setting the specimens were removed from the moulds and air-dried for a further 24-hour period. 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.

At the later stage of this work, each cement-bonded specimen was enclosed in an aluminum container to prevent complete or partial hydration of cement by the calorimeter water. To accomplish this, the air-dried cement-bonded specimen was crushed to pass an 8-mesh Tyler screen. The crushed specimen was placed in a crucible and heated at 500°C to constant weight, cooled down to about 100°C, and tightly packed into a 1 1/8-in.-diameter and 5 1/4-in.-long aluminum container. The open end of the filled-up container was covered with an aluminum cap and sealed water-tight with aluminum solder.

Determination of Mean Specific Heats

(i) Method of Measurement

Of the numerous methods that are employed for specific heat measurements, the "method of mixtures" is generally acknowledged to be the most convenient and sufficiently accurate for the determination of the specific heats of fired ceramic products and rocks. In this method a specimen of the material under investigation, after being brought to a known temperature in a furnace, is dropped into a calorimeter which, operating near room temperature, measures the heat the specimen evolves in cooling to the calorimeter temperature. 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.

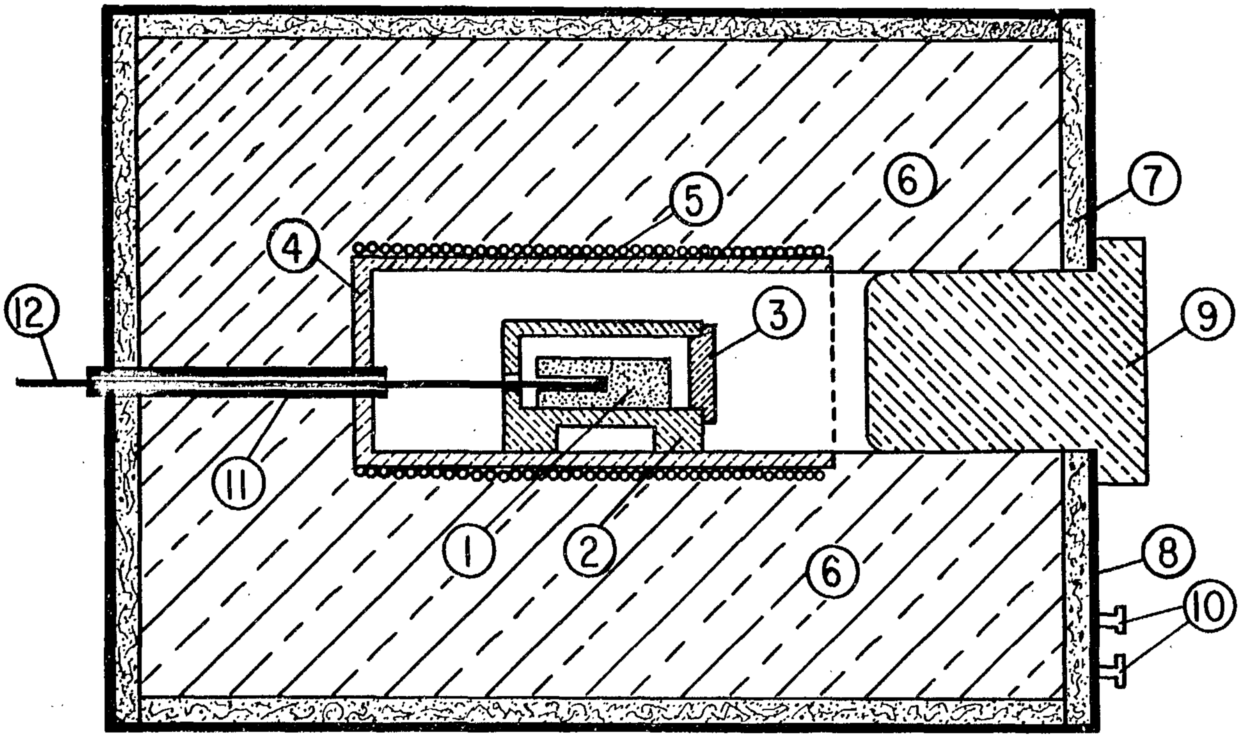
(ii) Electric Furnace

The central part of the furnace is shown in Figure 1. It consisted of a 14-in.-long, 7 1/2 in.-wide and 5 1/2-in.-high refractory muffle. The muffle was wound externally with a coiled 12 B&S gauge Chromel "A" (Cr 20%, Ni 80%) wire. The power consumption of the heating element was 3.4 kilowatts at 115 volts. The muffle was set horizontally inside a transite box, and was well insulated to ensure uniformity of temperature within the muffle. A 6-in.-thick, tightly fitting door was used to close a 5 1/2 in. x 7 1/2 in. opening in the front of the furnace.

(iii) Calorimeter

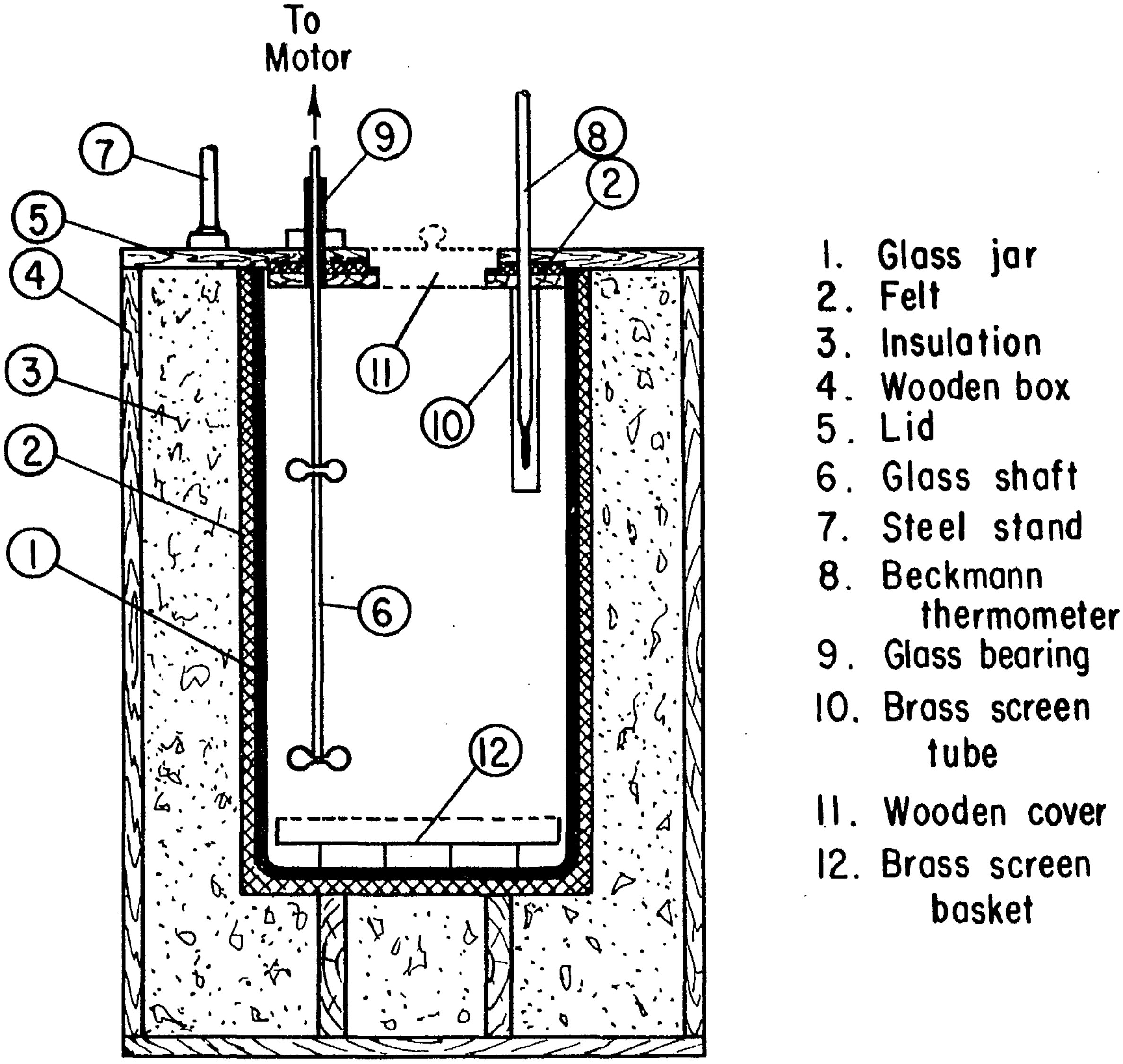
The calorimeter shown in Figure 2, consisted of a 12-in.-diameter, 24-in.-high glass jar having about a 39,000-ml capacity. It was inclosed in a wooden case and well insulated. The top of the calorimeter was covered with an insulated wooden lid. The stirring arrangement consisted of a glass shaft with two propellers driven by a small electric motor.

Heated 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. The latter was removed only for a short period when the specimen was dropped into the calorimeter.



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.



1. Glass jar
2. Felt
3. Insulation
4. Wooden box
5. Lid
6. Glass shaft
7. Steel stand
8. Beckmann thermometer
9. Glass bearing
10. Brass screen tube
11. Wooden cover
12. Brass screen basket

FIGURE 2. CALORIMETER.

The rise in temperature of the water was measured with a Beckmann thermometer.

(iv) Heat Capacity of the Calorimeter

An important factor encountered in all specific-heat determinations is the heat capacity of the calorimeter system. Initially, 34,000 ml of distilled water was accurately measured and transferred to the calorimeter jar. The heat capacity of the calorimeter system was determined by inserting a copper vessel containing a weighed quantity of hot water into the calorimeter water. The quantity of the hot water was 1000 ml and its temperature was 60°C. This was sufficient to produce a rise in temperature of the calorimeter system of about 1°C. The precise temperature rise in the calorimeter water was obtained as in a normal specific heat determination, that will be described later.

(v) Procedure for Determination of Mean Specific Heats

The specimen of the material, on which the mean specific heat was to be determined, was kept at 500°C for about an hour to remove absorbed water, then cooled to room temperature in a desiccator and weighed. The weighed specimen was put in a 6 in. x 2 in. x 2 in. ceramic container made from insulating brick or semi-porcelain body. The container was closed by a ceramic plug and placed in the muffle of the furnace as shown in Figure 1.

In the early stage of this work the furnace was controlled manually. It was heated up to about 430°C and maintained at this temperature constantly. When a specimen was placed in the furnace the temperature of the furnace was slowly raised from 430°C to the final heating temperature. The temperature of the specimen was measured by a calibrated chromel-alumel thermocouple which was inserted into the thermocouple hole of the specimen, through a small opening in the back of the furnace and in the ceramic container.

At the later stage of this work the temperature of the furnace was controlled by a Honeywell Proportioning Controller. To reduce the error of the proportioning controller, a constant-voltage transformer was used to eliminate the voltage fluctuation of the 115-volt mains. A calibrated chromel-alumel thermocouple of the controller was imbedded into the wall of the furnace muffle. Once the furnace was heated up to the desired temperature it remained constantly at this temperature, except for very short intervals when a specimen was placed in or removed from the furnace. The temperature of the specimen, which at this stage of the investigation was sealed in an aluminum cylinder, was measured outside of the ceramic container holding the aluminum cylinder. Two calibrated chromel-alumel thermocouples were placed approximately in the middle of the furnace muffle, on opposite sides of the ceramic container. In both stages of the work a Leeds and Northrup portable potentiometer was used that could be read directly to 0.01 millivolt.

In order to attain the maximum uniformity of heat distribution, the specimens were kept in the furnace at top heating temperature for four hours. Towards the end of this heating period, the water in the calorimeter was stirred and the temperature of the water observed on the Beckmann thermometer every minute. When the rate of change in temperature was constant in the calorimeter for ten minutes, the heated specimen was quickly transferred from the furnace to the calorimeter. This was done in less than 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 the operation was discontinued. The exact temperature rise in the calorimeter water was obtained graphically when the curves showing the constant rates of change before and after dropping the heated specimen were plotted.

The mean specific heat between the temperatures 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,

C = mean specific heat of specimen between T_s and T.

For specimens that were enclosed in aluminum cylinders, a correction was applied to the values of T for the effect of the sealed, empty cylinder. This was determined from blank runs to be $0.003^{\circ}C/g$.

Accuracy of the Apparatus and of the Experimental Technique

(i) Apparatus

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

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. With the aid of a thermometer reading lens the readings were estimated to 0.001°C and the necessary corrections were applied.

Satisfactory uniformity of temperature throughout the specimen in the furnace was achieved by using a large, well-insulated furnace. The ceramic specimen-holder distributed the heat more evenly throughout the specimen. When the furnace temperature was controlled manually, the fluctuation in power input caused a temperature variation of ±2°C. With an automatic control arrangement, no change in temperature in the furnace could be detected for the time interval which was necessary to attain the maximum heat distribution throughout the specimen (4 hours).

(ii) Experimental Technique

The time required to transfer a specimen from the furnace to the calorimeter was approximately four to six seconds. 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 distance through which the specimen fell from the container into the water of the calorimeter was about four inches. 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.[16]

One uncertainty in specific heat determination was the amount of heat transferred between the calorimeter and its environment. 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.

In the determination of the heat capacity of the calorimeter system, the copper cylinder, with or without water, was heated in a large water bath which was maintained at a 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

The bulk densities and apparent specific gravities of the ceramic products, ceramic bodies and ceramic-rock bodies were determined and calculated as prescribed in the ASTM Standard C20-46.

True Density of Rocks

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

EXPERIMENTAL RESULTS

Ceramic Products and Ceramic Bodies

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 all compiled in Tables 6, 7 and 8. The temperature intervals in which the mean specific heats were determined are also given. Since the ceramic products and the ceramic bodies are more or less porous materials, each heat capacity per unit volume is given as the product of the bulk density and the mean specific heat.

The specimens of ceramic bodies A and B (except the specimens of body A_5), shown in Tables 7 and 8, were not enclosed in aluminum cylinders when their specific-heat values were determined. As a result, the mean specific-heat values of these unprotected bodies containing aluminous cement are too high by about 0.008 cal/g. °C, as determined experimentally. This extra heat is due to the hydration of aluminous cement when the specimen is dropped in the calorimeter water. As the same amount of aluminous cement was used for all A and B body compositions, the results were considered satisfactory for comparison.

TABLE 6

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

SAMPLE	T_s, °C	T, °C	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	456.1	26.6	0.240	3.04	3.84	0.730
Periclase Brick	456.1	27.0	0.258	3.00	3.51	0.774
Magnesite Brick	456.1	26.6	0.256	2.54	3.11	0.650
Silica Brick	456.1	26.3	0.231	1.80	2.36	0.416
Fireclay Brick	456.1	26.4	0.227	1.83	2.48	0.415
Building Brick	456.1	26.2	0.222	2.03	2.58	0.451
Magnesite Clinker	500.2	26.1	0.263	3.17	3.28	0.834
Chrome-Magnesite Brick, crushed	500.0	26.5	0.221	2.86	3.79	0.632
Aluminous Cement Clinker	502.2	27.0	0.211	3.10	3.18	0.654
Aluminous Cement	501.5	26.7	0.211	1.44	-	0.304

TABLE 7

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

BODIES		T_s, °C	T, °C	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% Aluminous cement 25%	456.0	26.6	0.262	2.42	3.40	0.634
A_2	Chrome-magnesite 75% Aluminous cement 25%	456.0	26.5	0.228	2.46	3.49	0.561
A_3	Fireclay brick 75% Aluminous cement 25%	456.0	26.2	0.229	1.78	2.69	0.408
A_4	Building brick 75% Aluminous cement 25%	456.0	26.2	0.230	1.68	2.71	0.386
A_5	Aluminous cement clinker 75% Aluminous cement 25%	501.2	27.2	0.210	2.53	3.30	0.531

TABLE 8

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

BODIES		T_s, °C	T, °C	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 & T, cal/cm^3.°C
Code	Compositions						
B_1	Magnesite clinker* 25% Chrome-magnesite 50% Aluminous cement 25%	456.1	26.5	0.235	2.44	3.46	0.573
B_2	Magnesite clinker 25% Fireclay brick 50% Aluminous cement 25%	456.1	26.4	0.243	2.01	2.91	0.488
B_3	Magnesite clinker 25% Building brick 50% Aluminous cement 25%	456.1	26.7	0.246	1.89	2.95	0.465
B_4	Magnesite clinker 50% Chrome-magnesite 25% Aluminous cement 25%	456.1	30.3	0.237	2.45	3.44	0.581
B_5	Magnesite clinker 50% Fireclay brick 25% Aluminous cement 25%	456.1	26.3	0.250	2.30	3.23	0.575
B_6	Magnesite clinker 50% Building brick 25% Aluminous cement 25%	456.1	26.3	0.255	2.08	3.19	0.530
B_7	Chrome-magnesite 25% Fireclay brick 50% Aluminous cement 25%	456.1	27.1	0.236	1.99	2.94	0.470
B_8	Chrome-magnesite 50% Fireclay brick 25% Aluminous cement 25%	456.1	26.4	0.234	2.23	3.06	0.522

* Dead-burned magnesia.

Rocks and Ceramic-Rock Bodies

The mean specific heats, the true densities and the heat capacities, that were obtained on the rock samples, are compiled in Table 9. Because the results of the first fifteen rock samples (Nos. 1 to 15) were also used for another project, their mean specific heats were determined over the range of 27.0° to 625°C. This procedure was considered satisfactory for the requirements of this investigation. In order to prevent eventual dissociation, particularly of magnesium carbonate, the thermal properties of five carbonate-rock samples (Nos. 16 to 20) were determined over the range of 26.7° to 456°C. The mean specific heats of the last fourteen rock and two mineral-concentrate samples (Nos. 21 to 36) in Table 9 were determined over the range of 26.5° to 500°C. Since the porosities of most of the rocks examined are low, each heat capacity per unit volume is given as the product of the true density and the mean specific heat.

The results obtained on the two- and three-component ceramic-rock bodies are given in Tables 10 and 11. The specimens of the first three bodies, C_1, C_2 and C_3, in Table 10 and the specimens of the six D bodies in Table 11 were in form of briquettes, and their specific-heat values were determined in the same manner as those of bodies A and B in Table 7 and 8. Here, again, the given mean specific-heat values of the above nine C and D bodies are too high by about 0.008 cal/g.°C. The specimens of nineteen bodies, shown in Table 10 and designated as C_4 to C_{22}, were enclosed in aluminum cylinders before their specific heats were determined. Prior to that, the rock constituents of bodies C_9, C_{13} to C_{18}, and C_{22} were pre-heated at 1000°C for one hour to expel the water of crystallization and the eventual

TABLE 9

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

SAMPLE		T_s, °C	T, °C	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	Physical Condition after One Hour Heating at 1000°C
No.	ROCKS AND MINERAL CONCENTRATES						
1	Albite Granite, M-195	625.0	27.1	0.241	2.650	0.639	Slightly friable
2	Anorthosite, M-193	625.0	27.3	0.234	2.825	0.661	Slightly weaker
3	Sandstone, M-176	625.0	26.8	0.246	2.657	0.654	Slightly friable
4	Gabbro (Diabasic), M-178	625.0	27.0	0.227	2.978	0.676	Quite strong
5	Nepheline Syenite, M-188	625.0	26.9	0.237	2.632	0.624	Not heated
6	Basalt, M-189	625.0	27.4	0.236	3.043	0.718	Hard and strong
7	Rhyolite, M-190	625.0	26.7	0.237	2.664	0.631	Not heated
8	Syenite, M-191	625.0	27.1	0.229	2.637	0.604	Not heated
9	Nordmarkite, M-192	625.0	27.0	0.231	2.660	0.614	Not heated
10	Granite, M-194	625.0	27.0	0.238	2.649	0.630	Not heated
11	Granodiorite, M-208	625.0	26.8	0.237	2.766	0.656	Very friable, disintegrated
12	Granite, M-209	625.0	27.1	0.237	2.660	0.630	Not heated
13	Quartz Monzonite, M-210	625.0	26.8	0.240	2.676	0.642	Not heated
14	"Quartz Rock", M-179	625.0	26.5	0.250	2.660	0.665	Disintegrated
15	Quartzite, M-207	625.0	26.8	0.249	2.665	0.664	No change
16	Limestone, M-184	456.0	26.6	0.241	2.728	0.657	Soft and friable
17	Limestone (Recrystallized), M-185	456.0	26.7	0.241	2.740	0.660	Soft and friable
18	Magnesian Limestone, M-187	456.0	26.6	0.243	2.752	0.669	Very soft and friable

(Continued)

TABLE 9 (cont'd)

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

SAMPLE		T_s, °C	T, °C	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	Physical Condition after One Hour Heating at 1000°C
No.	ROCKS AND MINERAL CONCENTRATES						
19	Dolostone, M-186	456.0	26.8	0.251	2.500	0.628	Very weak and friable
20	Dolostone, M-168	456.0	26.6	0.253	2.856	0.722	Very soft and friable
21	Microsyenite	500.1	26.2	0.224	3.078	0.689	No change
22	Olivine	501.1	27.4	0.243	3.331	0.809	Very hard
23	Dumortierite	501.2	26.2	0.248	2.981	0.735	Relatively strong
24	"Talc", dark	500.0	26.7	0.280	2.832	0.792	Very hard
25	Talc, dark-grey	500.0	26.3	0.253	2.942	0.744	Hard
26	Talc, light-grey	500.0	26.6	0.254	2.857	0.726	Hard
27	Serpentine, dark-green	499.8	26.8	0.286	2.500	0.715	Disintegrated
28	Serpentine, light-green	500.3	26.8	0.290	2.600	0.777	Disintegrated
29	Amphibole, #420	501.1	26.2	0.211	3.867	0.816	Friable
30	Specular Hematite, Ontario	500.0	26.2	0.220	3.690	0.812	No change
31	"Iron Formation"	501.0	26.4	0.232	2.837	0.658	No change
32	Amphibolite	500.0	26.2	0.226	3.266	0.738	No change
33	Specular Hematite, Labrador	501.2	26.2	0.212	3.405	0.723	Not heated
34	Hematite Concentrate, Labrador	500.9	26.1	0.193	4.991	0.963	Not heated
35	Hematite Super-concentrate	500.4	26.3	0.193	5.293	1.022	Not heated
36	Magnetite Ore, CM-323	500.2	26.4	0.210	4.240	0.840	Hard and strong. Some minor cracks.

TABLE 10

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

BODIES		T_s, °C	T_o, °C	Mean Specific Heat between T_s and T_o cal/g. °C	Bulk Density, g/cm^3	Apparent Specific Gravity	Heat Capacity Per Unit Volume between T_s and T_o cal/cm^3. °C	Physical Condition after One Hour Heating at 1000°C
Code	Compositions							
C_1	Quartzite, M-207 75% Aluminous cement 25%	456.0	26.2	0.246	1.99	2.69	0.490	Hard and strong. Suitable for blocks.
C_2	Sandstone, M-176 75% Aluminous cement 25%	456.0	26.3	0.245	1.99	2.76	0.488	Hard and strong. Suitable for blocks.
C_3	Granite, M-195 75% Aluminous cement 25%	456.0	26.3	0.245	1.99	2.77	0.488	Sufficiently strong. Can be used for blocks.
C_4	Anorthosite, M-193 75% Aluminous cement 25%	500.5	26.6	0.232	2.24	2.78	0.520	Very hard and strong. Suitable for blocks.
C_5	Gabbro, M-178 75% Aluminous cement 25%	500.0	26.4	0.216	2.39	2.94	0.516	Hard and strong. Suitable for blocks.
C_6	Basalt, M-189 75% Aluminous cement 25%	500.0	26.6	0.221	2.35	2.97	0.519	Hard and strong. Suitable for blocks.
C_7	Microsyenite 75% Aluminous cement 25%	500.0	26.5	0.222	2.34	2.88	0.519	Hard and strong. Suitable for blocks.
C_8	Olivine 75% Aluminous cement 25%	501.0	26.9	0.235	2.56	3.13	0.602	Hard and strong. Suitable for blocks.
C_9	Dumortierite (Pre-calcined at 1000°) 75% Aluminous cement 25%	502.0	25.0	0.233	2.12	2.65	0.493	Very weak and friable. Not suitable for blocks.
C_{10}	"Talc", dark 75% Aluminous cement 25%	501.9	26.4	0.269	1.90	2.74	0.511	Hard and strong. Suitable for blocks.
C_{11}	Talc, dark-grey 75% Aluminous cement 25%	502.0	26.6	0.247	1.87	2.76	0.462	Hard and sufficiently strong. Can be used for blocks.

(Continued)

TABLE 10 (cont'd)

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

BODIES		T_s, °C	T, °C	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	Physical Condition after One Hour Heating at 1000°C
Code	Compositions							
C_{12}	Talc, light-grey 75% Aluminous cement 25%	502.0	26.6	0.248	1.89	2.76	0.469	Hard and strong. Suitable for blocks.
C_{13}	Serpentine, dark-green (pre-calcined at 1000°C) 75% Aluminous cement 25%	500.1	26.8	0.260	1.93	2.52	0.502	Very weak. Not suitable for blocks.
C_{14}	Serpentine, light-green (pre-calcined at 1000°C) 75% Aluminous cement 25%	499.5	27.0	0.243	1.97	2.54	0.479	Strong enough to be used for blocks.
C_{15}	Amphibole #420 (pre-calcined at 1000°C) 75% Aluminous cement 25%	499.8	26.5	0.208	2.79	3.49	0.580	Hard and strong. Suitable for blocks.
C_{16}	Specular hematite, Ontario (pre-calcined at 1000°C) 75% Aluminous cement 25%	500.0	26.3	0.214	2.85	3.39	0.610	Hard and strong. Suitable for blocks.
C_{17}	"Iron Formation" (pre-calcined at 1000°C) 75% Aluminous cement 25%	500.0	26.5	0.228	2.35	2.78	0.536	Hard and strong. Suitable for blocks.
C_{18}	Amphibolite (pre-calcined at 1000°C) 75% Aluminous cement 25%	501.5	26.4	0.222	2.51	3.00	0.557	Hard and strong. Suitable for blocks.
C_{19}	Specular hematite, Labrador 75% Aluminous cement 25%	500.5	26.5	0.224	2.49	3.24	0.558	Hard and strong. Suitable for blocks.
C_{20}	Hematite conc., Labrador 75% Aluminous cement 25%	500.0	26.5	0.200	3.26	4.05	0.652	Hard and strong. Suitable for blocks.
C_{21}	Hematite super-conc. 75% Aluminous cement 25%	500.3	26.4	0.200	2.99	4.05	0.598	Hard and strong. Suitable for blocks.
C_{22}	Magnetite ore, CM-323 (pre-calcined at 1000°C) 75% Aluminous cement 25%	500.0	26.2	0.197	2.90	3.59	0.571	Hard and strong. Suitable for blocks.

TABLE 11

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

BODIES			T_s, °C	T, °C	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							
D_1	Magnesite clinker Quartzite, M-207 Aluminous cement	50% 25% 25%	456.0	26.6	0.258	2.24	3.01	0.578
D_2	Magnesite clinker Quartzite, M-207 Aluminous cement	25% 50% 25%	456.0	26.5	0.255	2.08	2.83	0.530
D_3	Magnesite clinker Sandstone, M-176 Aluminous cement	50% 25% 25%	456.0	26.5	0.257	2.28	3.06	0.586
D_4	Magnesite clinker Sandstone, M-176 Aluminous cement	25% 50% 25%	456.0	26.5	0.252	2.14	2.92	0.539
D_5	Magnesite clinker Granite, M-195 Aluminous cement	50% 25% 25%	456.0	26.4	0.258	2.31	3.11	0.596
D_6	Magnesite clinker Granite, M-195 Aluminous cement	25% 50% 25%	456.0	26.4	0.248	2.15	2.89	0.533

gases from minerals.

DISCUSSION OF RESULTS

Ceramic Products and Ceramic Bodies

(i) Ceramic Products

The data in Table 6 indicate that the mean specific-heat and the heat-capacity values of the high-alumina and the periclase brick are superior to the rest of the bricks investigated; the periclase brick has the highest mean specific-heat and heat-capacity values. The magnesite brick has almost the same mean specific heat as the periclase brick, but its bulk density is lower. Consequently, the heat capacity of the magnesite brick is lower. The silica, the fireclay, and the building brick have lower mean specific heats and heat capacities than the former three ceramic products.

The mean specific-heat and the heat-capacity values of the dead-burned magnesia (magnesite clinker) indicate that this ceramic product is an excellent constituent for ceramic-body compositions. The mean specific heat of the aluminous-cement clinker is as low as that of the aluminous cement. However, the bulk density of aluminous-cement clinker is high and the heat capacity of it is similar to that of the magnesite brick. The mean specific heat of the chrome-magnesite brick is slightly higher than that of the aluminous-cement clinker and the heat-capacity value of this brick is very close to the heat-capacity values of the magnesite brick and the aluminous-cement clinker.

(ii) Two- and Three-Component Ceramic Bodies

The results compiled in Tables 7 and 8 show 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 specimens of bodies A and B, except the specimens of body A_5, were not enclosed in aluminum cylinders when their specific heats were determined.

Ceramic body A_1 in Table 7 consists of magnesia clinker and aluminous cement in the ratio 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 magnesia clinker in their compositions, and their mean specific-heat and heat-capacity values are low. Body A_5 also does not contain magnesia clinker and its mean specific heat is the lowest. However, the density of the body A_5 is quite high and the heat capacity is close to that of the body A_2.

The results shown in Table 8 follow the same general trend as do the results reported in Table 7, 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 aluminous cement in the ratio of 1:2:1) has relatively high heat capacity. If the magnesia in the chrome-magnesite brick is taken into consideration, 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 lowering 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. Consequently, their heat capacities are inferior to that of body B_1. Three-component ceramic bodies with a heat capacity similar to that of B_1 can be prepared, if magnesite clinker and aluminous cement 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 aluminous cement, in the ratios of 1:2:1 and 2:1:1, produced results indicated for bodies B_7 and G_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.

Rocks and Ceramic-Rock Bodies

(i) Rocks

The thermal properties of the first fifteen rock samples, listed in Table 9 from Nos. 1 to 15, are inferior to those obtained on the dead-burned magnesia, the periclase brick and the high-alumina 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 over the range of 26.5° to 500°C. Basalt M-189 (No. 6), Gabbro M-178 (No. 4), Quartz Rock M-179 (No. 14), Quartzite M-207 (No. 15), Anorthosite M-193 (No. 2), Granodiorite M-208 (No. 11), Sandstone M-176 (No. 3), and Albite Granite M-195 (No. 1) all have relatively high heat capacities and were considered good constituents for ceramic-rock bodies. Before the final selection, samples of the above rocks were heated at 1000°C for one hour. Such a temperature could be reached in the vicinity of electrical heating elements if the rocks were used as thermal-storage media, and a decrease in strength, or even decomposition, may take place. The results of the heating are shown in the last column of Table 9; only six of the eight selected rocks, such as Basalt M-189 (No. 6), Gabbro M-178 (No. 4), Quartzite M-207 (No. 15), Anorthosite M-193 (No. 2), Sandstone M-176 (No. 3) and Albite Granite M-195 (No. 1), turned out to be suitable constituents for ceramic-rock bodies. The thermal properties of the rest of the first fifteen rocks in Table 9 are lower and could be compared with those of the bodies A_1 and A_2 in Table 7 and the bodies B_1, B_4 and B_5 in Table 8.

The thermal properties of the five carbonate-rock samples, shown in Table 9 from No. 16 to 20, appeared to be similar to the six best rock samples previously discussed, i.e. Nos. 1, 2, 3, 4, 6 and 15. As was indicated before, 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 (No. 20), for example, has thermal properties that are very close to those of the magnesite brick in Table 6. Notwithstanding their excellent thermal properties, the carbonate rocks have a deficiency as thermal-storage media. When such materials are heated to higher temperature, dissociation takes place. This may happen in the vicinity of electrical heating elements. The calcined part hydrates, on cooling, by picking up air moisture and this causes disintegration of the body. This shortcoming could be avoided if stabilized materials, such as stabilized dolomite, were used.

The thermal properties of most of the last fourteen rock and two mineral-concentrate samples, shown in Table 9 from No. 21 to 36, are superior to those obtained on the high-alumina brick and the periclase brick; the heat capacities of some are even higher than that of the dead-burned magnesia. Both Hematite concentrates (No. 34 and 35), Magnetite Ore CM323 (No. 36), Amphibole #420 (No. 29), Specular Hematite, Ontario (No. 30), with high percentage of hematite and/or magnetite in their compositions, as well as Olivine (No. 22) and "Talc" dark (No. 24) containing forsterite and chlorite respectively, have particularly high heat capacities. As before, thirteen rock samples were heated at 1000°C for one hour prior to their selection as constituents for ceramic-rock bodies. The results of the heating are once again shown in the last column of Table 9. Ten rock samples were not affected by the heating and were considered good aggregates for ceramic-rock bodies. Samples of Serpentine No. 27 and No. 28 disintegrated and the sample of Amphibole #420 (No. 29) was quite friable. Considering the mean specific-heat values of both serpentine samples and the density and the composition of the Amphibole #420 (No. 29), they were also selected as satisfactory aggregates if calcined prior to use for ceramic-rock bodies. Samples of Specular Hematite, Labrador (No. 33) and two Hematite concentrates (No. 34 and 35) were used in ceramic-rock bodies "as received". Their mineralogical analyses indicated that temperatures up to 1000°C will not affect their strength.

(ii) Two-Component Ceramic-Rock Bodies

The thermal properties of twenty-two two-component ceramic-rock bodies shown in Table 10 and designated from C_1 to C_{22} are lower than those of pure-rock samples. Bodies C_8, C_{15}, C_{16}, C_{18}, C_{19}, C_{20}, C_{21} and C_{22}, containing hematite, magnetite and/or magnesium silicates, have higher thermal properties than the rest of the C bodies, which do not have the above minerals in any appreciable amount in their rock constituents. The mean specific heats of these eight C bodies are relatively low. However, their bulk densities are high and therefore their heat capacities per unit volume are high. In contrast with that, the mean specific-heat value of body C_{10} is the highest shown in Table 10, but C_{10}'s bulk density is one of the lowest. Hence the heat capacity of the body C_{10} is only moderate. By comparing the thermal properties of bodies A in Table 7 with those of bodies C in Table 10, it can be seen that the thermal properties of the latter are generally superior. For example, bodies C_{16}, C_{20}, C_{21} and C_{22}, being rich in hematite or magnetite, are just as effective as body A_1; bodies C_8, C_{15}, C_{18}, and C_{19} can successfully substitute for bodies A_2 and A_5. Furthermore, the results indicate that in two-component ceramic-rock bodies consisting of a filler and aluminous cement in the ratio 3:1, the twenty rocks and two mineral concentrates listed in Table 10 are more effective fillers than the fireclay brick and the building brick (Table 7). The mechanical strength of eighteen C bodies was excellent after one hour heating at 1000°C; two others, C_3 and C_{14}, were only moderately strong. Bodies C_9 and C_{13} were weak and friable and therefore not suitable as thermal-storage media for block heaters.

(iii) Three-Component Ceramic-Rock Bodies

The results compiled in Table 11 prove once again that the bodies with high magnesite clinker content have high thermal properties. The three-component body D_1, consisting of magnesite clinker, quartzite, and aluminous cement in the ratio of 2:1:1, has high mean specific heat and relatively high heat capacity. 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 bodies D_3, D_4, D_5 and D_6. The heat capacities per unit volume of the three-component ceramic-rock bodies D generally approach but does not exceed that of the best C bodies in Table 10. By comparing the thermal properties of bodies B_2 and B_3 in Table 8 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 aluminous cement in the ratio of 1:2:1, the fireclay brick (or building brick) might be successfully replaced by quartzite, sandstone, granite and similar rock fillers.

SUMMARY

By means of a calorimeter, using water, it has been established that the samples of ceramic products and ceramic bodies have mean specific heats ranging from 0.210 to 0.263 cal/g.°C, and heat capacities per unit volume ranging from 0.304 to 0.834 cal/cm³.°C, over the range of 26.5° to 456° (500°)C.* It was also established that the samples of fifteen rocks have mean specific heats ranging from 0.227 to 0.250 cal/g.°C, and heat capacities per unit volume ranging from 0.604 to 0.718 cal/cm³.°C, over the range of 27.0° to 625°C; and that samples of twenty-one rock and ceramic-rock bodies have mean specific heats ranging from 0.193 to 0.290 cal/g.°C, and heat capacities from 0.462 to 1.022 cal/cm³.°C, over the range of 26.5° to 500° (456°)C.**

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

1. Dead-burned magnesia (over 95% MgO) and 'highly calcined' alumina (over 99% Al_2O_3) have high mean specific heats. Having high bulk densities, both materials have also high heat capacities.

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* Mean specific heats of four ceramic products (Table 6), and of one two-component ceramic body (Table 7), were determined over the range of 26.5° to 500°C.

** Mean specific heats of rocks Nos.16 to 20 (Table 9) were determined over the range of 26.7° to 456°C.

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

3. The chrome-magnesite brick and the aluminous-cement clinker have the lowest mean specific-heat values of all the ceramic products examined. However, their bulk densities are high and the heat capacities per unit volume of the chrome-magnesite brick and the aluminous-cement clinker are practically the same as that of the magnesite brick.

4. The thermal properties of the two- and the three-component ceramic bodies are inferior to those of dead-burned magnesia and 'highly calcined' alumina. Dead-burned magnesia with aluminous cement, 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-heat and the heat-capacity values of the two-component bodies are lowered when the dead-burned magnesia is replaced by chrome-magnesite, fireclay brick, or building brick. Aluminous-cement clinker with aluminous cement, in the ratio of 3:1, has a low mean specific-heat value. However, the heat capacity per unit volume of this two-component body is as high as that of the body made from chrome-magnesite brick with aluminous cement.

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

5. Of the thirty-four rocks investigated, eleven have higher thermal properties than those of 'highly calcined' alumina, and might be considered effective substitutes for the latter. Two hematite concentrates, and the rocks that have a high percentage of hematite, magnetite and/or magnesian compounds in their compositions, have particularly high heat capacities and might even successfully replace dead-burned magnesia in ceramic-rock bodies. Rocks such as basalt, gabbro, quartzite, anorthosite, sandstone and granite have better thermal properties than those of the fireclay brick and the building brick, and can effectively replace them in some body compositions.

The five carbonate rocks have thermal properties superior to those of basalt, gabbro and quartzite. The mean specific heat and the heat capacity of dolostone are close to the thermal properties of the periclase brick. However, only stabilized dolostone might be considered an effective substitute for dead-burned magnesia.

6. The two-component and three-component ceramic-rock bodies have lower mean specific-heat and heat-capacity values than have the pure rock samples. Two-component ceramic-rock bodies that contain

hematite, magnetite and/or magnesian compounds have higher heat capacities per unit volume than the bodies that do not contain such constituents; similarly, three-component ceramic-rock bodies with high dead-burned magnesia content have high mean specific heats and high heat capacities. Any attempt to reduce the dead-burned magnesia content in the three-component ceramic-rock bodies lowers the values of these thermal properties.

The electrical properties of the thermal-storage media investigated were not measured, although it is possible that some of the ceramic products, rocks and their compositions would be electrically conductive, particularly at higher operating temperatures. In this work it was assumed that the electrical heating elements of the heat-storage blocks are insulated from the thermal-storage media. If, however, the electrical heating elements are placed in direct contact with the thermal-storage media, the electrical resistivity of the latter should be taken into consideration to avoid possible electrical breakdown of the heat-storage blocks. To evaluate the thermal-storage media from this aspect a further systematic study is required.

CONCLUSIONS

The investigation has provided evidence that, of the ceramic products examined, the dead-burned magnesia and 'highly calcined' alumina have the best specific heats and heat capacities. Hematite concentrate, and rocks rich in hematite, magnetite and/or magnesian compounds, have higher heat capacities than have 'highly calcined' alumina and even dead-burned magnesia. Two- and three-component bodies made from ceramic products, or ceramic products and rocks bonded with aluminous cement, are economically more attractive and practical but have lower heat capacities than have hematite concentrates, hematite- and/or magnetite-containing rocks, and dead-burned magnesia and its products.

Within the scope of this work, it is concluded that materials and material compositions rich in hematite, magnetite, and magnesian compounds are excellent thermal-storage media, costing less than other materials and material compositions having similar heat capacities. Reduction of any of the above materials in the body compositions reduces the heat capacities of the bodies and, consequently, their value as thermal-storage media for block-type electric space heaters.

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