

CERAMICS FOR ENERGY STORAGE UNITS: BRICKS FROM NORTH CAROLINA OLIVINE FOR HEAT STORAGE FURNACES

H. PALMOUR III and B. M. GAY

Engineering Research Services Division, North Carolina State University,
Raleigh, North Carolina 27650 U. S. A.

I. H. REDEKER

Minerals Research Laboratory, North Carolina State University,
Asheville, North Carolina 28801 U. S. A.

ABSTRACT

High heat capacity refractory ceramics have been employed in European electric heat storage furnaces for some years. However, this kind of energy storage, and selection of suitable ceramics for it, has only recently begun to attract technological interest in the U. S. Because of its relatively high heat capacity and relatively low cost, olivine is one of the most attractive candidate materials for such ceramics, and North Carolina has extensive but rather under-utilized deposits of refractory grade olivine. This paper reports work undertaken under a grant from the North Carolina Energy Institute to investigate and demonstrate the suitability of North Carolina olivine in heat storage brick applications. It includes (1) the occurrence, availability and properties of North Carolina olivines, (2) selection, development and evaluation of refractory ceramic compositions of two different bond types, (3) evaluations of thermal properties, (4) processing and fabrication of full size prototype brick shapes, (5) comparisons of their properties with European units, and (6) evaluation of relative in-service performance.

INTRODUCTION

Heat storage units permit electrical load-leveling which enables power generating plants to operate more efficiently, thus contributing to better overall energy utilization. The principal application now envisioned for these ceramic heat reservoirs is in home or business heating (furnaces, space heaters). The primary objective of the study reported here has been to demonstrate that an important North Carolina mineral resource, olivine, can be used to make heat storage bricks (refractory ceramic shapes) of quality equal to (perhaps better than) those manufactured and used for such applications in Europe.

BACKGROUND

General considerations

Energy conservation has become a prime concern throughout the world. This is true for all forms of energy, but conservation of electrical energy has become particularly important to maintenance of personal, civic and national economies and life styles. Already excessive peak power loads and low usage during off-peak periods in the U. S. have necessitated the installation of generating equipment that is not efficiently utilized, thus driving up the cost of electricity and creating problems for the utility and the consumer alike.

One way to help offset this complex supply-demand problem is by the use of heat storage units for residential heating. Heat storage units have been in use in Europe for two decades. North Carolina's interest in them is centered in part on better utilization of electric energy per se but also in part on the refractory shapes employed as the ceramic heat reservoir (for convenience described herein as "bricks".) Western North Carolina has large deposits of olivine (a magnesium-iron orthosilicate mineral) which are the principal sources of domestic olivine available within the U. S. Ceramics made from olivine have high density, high heat capacity, high thermal conductivity, low thermal expansion and good strength characteristics. All of these qualities make olivine almost ideally suited for the economical production of bricks for heat storage applications. Technologically, North Carolina is also a traditional center within the U. S. for ceramic manufacturing, particularly for brick, tile and other structural clay products, more recently for glass, and for a variety of other products. At this time, olivine bricks for heat storage furnaces are not made commercially in the U. S. so they must be imported from Europe; thus making the cost of the bricks and heat storage units almost prohibitive. The use of North Carolina olivine in heat storage units is being studied now in preparation for an almost certain time when either lower off-peak rates or much higher peak rates, or increasing unavailability of traditional fossil fuels for home heating, will clearly encourage (perhaps even require) the use of ceramic based heat storage units in North Carolina and elsewhere in the U. S.

Heat storage furnaces

Storing heat for residential purposes is not really new: American colonists long ago heated bricks or rocks for personal use as bed or foot-warmers. But for "bricks" which function as important components in an overall technico-economic system for balancing energy use, one must turn to European examples established some two decades ago. They use furnaces which are loaded with high heat capacity refractory shapes (typically magnesite or olivine) surrounded with insulation. The bricks are heated electrically with resistance elements to approximately 760°-916°C (1400°-1500°F) during night hours when the electric power demand is

lowest. During the day, an air delivery system circulates air through the heated refractories, dilutes it as necessary with cool air, and delivers heated air at the desired temperature to the residence, as required. A heat storage unit virtually eliminates the demand for electric power for residential heating during the hours of peak load. For the utility, it helps to eliminate the need for excessive generating capacities, and as a pure resistance load, does not contribute to excessive power factor losses. For the consumer, it tends to lower future electric power costs because it is not necessary to pay for construction of little-needed generating facilities. If the rate structure encourages the use of electricity during non-peak demand periods, the consumer can also realize an immediate savings on current electric bills.

The primary incentives are economic ones. In Europe, furnaces store heat during designated off-peak periods when electricity is less expensive and release it during designated peak periods when electricity costs more. Industrial, commercial and residential users are encouraged to use heat storage furnaces because they save money. Where heat storage systems are used extensively, electric demand is level--there are no real peaks. Ultimately, everyone wins!

Heat storage furnaces are new but not entirely unknown in the USA. A Johnson City, Tennessee firm, TPI, Inc., has purchased marketing rights for North and South America under a British heat storage furnace patent. The company is presently producing units for commercial and industrial use and plans to begin production of residential models for the 1979-1980 heating season. Similarly, a Vermont contractor has installed very compact (1-10 kw range) German residential heat storage systems in 106 homes. In that state, under a form of peak-load pricing, electricity costs 1.9¢ per kwh at night and 4.2¢ per kwh during the day. The furnaces save consumers money by storing heat at night and releasing it during the day. The Vermont contractor believes small heat storage "space heaters" may become popular there because of the number of older homes which lack the duct network necessary for central forced air heating.

Figure I shows typical heat storage furnace components for a central system based upon the English design. A sophisticated "brain" monitors temperatures inside the home as well as outside temperatures, measures the amount of heat in the storage bricks, predicts outside temperatures during the next release period and calculates how much additional heat must be stored and the percent of air that must be passed through the heat storage bricks to maintain the desired home temperature. The system works well except possibly during periods of extreme outside temperature change, when the stored heat may not be sufficient to maintain a comfortable inside temperature. In that case, an auxiliary (but more expensive) resistance heating system takes over until the bricks can again be brought up to the necessary temperature under the normal (low cost) off-peak recharging condition.

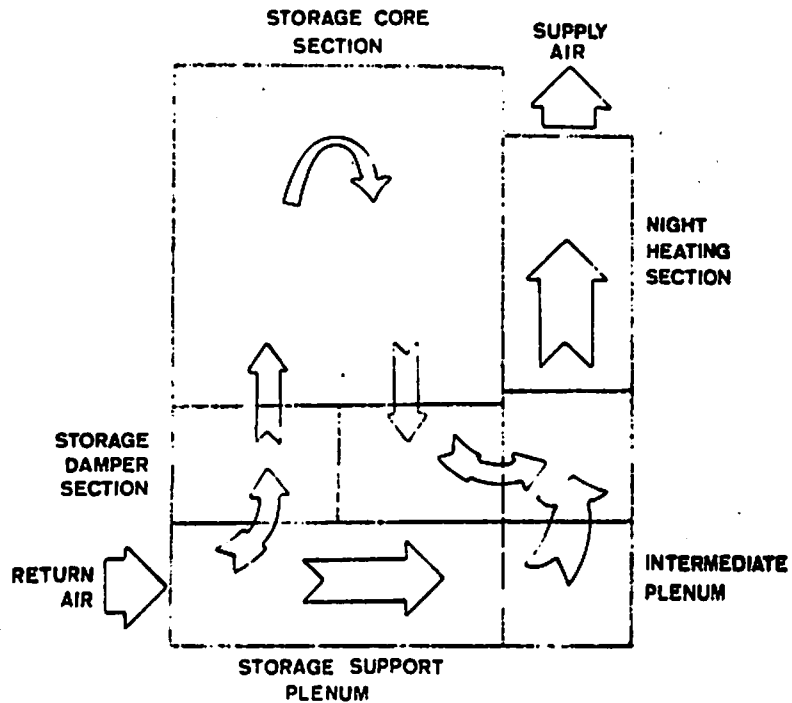


Fig. 1. Schematic of central system heat storage furnace showing direction of air flow.

The furnaces are somewhat larger than conventional fossil fuel fired home heating systems and require more surrounding air space because of higher surface temperatures. Installation costs are expected to be generally competitive with another energy conversion device, the so-called heat pump. Actual operating costs will depend upon peak load pricing policies and upon relationships between local climatic conditions and electrical energy demand patterns (e.g., regions with winter-peaking power demands will tend to favor the economical heat storage furnace, whereas summer-peaking areas may opt for the heat pump because of its optional air-conditioning mode).

Heat storage bricks must be specially shaped so that when they are placed together, they provide snug-fitting channels for the electric heating elements and also form baffles and conduits for air. Figure 2 illustrates these shape factors for the English-designed heat storage brick used in the TPI furnace which was selected for use in this demonstration study.

Olivine in North Carolina

Western North Carolina and contiguous portions of Northeast Georgia contain large reserves of high grade olivine in a number of dunite deposits. The mineral olivine is the main constituent of the rock dunite. The properties and uses are

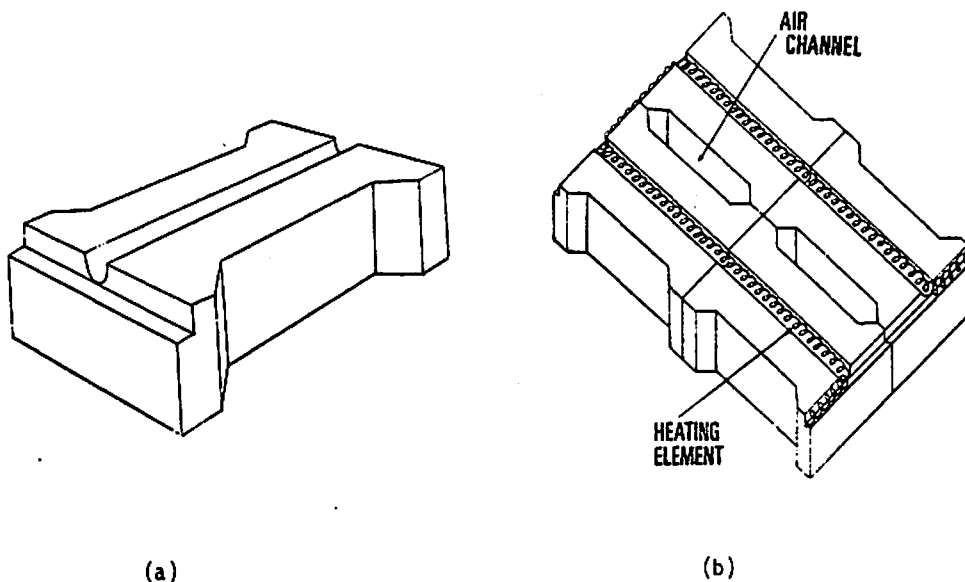


Fig. 2. Shape factors for the English-designed olivine heat storage brick: (a) individual brick measuring 248 x 165 x 83 mm (9.75 x 6.50 x 3.25 in) (b) portion of heat storage core, showing heating element and air channels.

well described in a number of publications (ref. 1-4). Olivine is a magnesium iron orthosilicate, a solid solution of forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). Olivine has at least 35% forsterite content. Dunite rocks also contain accessory minerals such as pyroxenes and chromite as well as certain typical hydrothermally altered and/or weathered minerals including serpentine, talc, chlorite, vermiculite and amphibole.

Hunter (ref. 5) states that deposits of olivine occur in a belt 175 miles long and 15 miles wide, extending from Watauga County, N. C., southwestward to White County, Ga., with Asheville, N. C. approximately at its center (Fig. 3). In 1941, he estimated that 20 of the largest and most accessible deposits contained 1,000,000,000 tons of dunite with over 40% MgO. He further estimated these deposits to contain 230,000,000 tons of high grade olivine ore averaging 48% MgO. Additional olivine deposits have been discovered and have become accessible in more recent years. At this time, there are three different North Carolina companies that mine and process olivine for refractory, foundry sand, blast furnace flux and blasting sand uses: (1) Northwest Olivine Company, with mines at Frank, Newdale, Green Mountain, Balsam Gap and Addie, and processing plants at Burnsville and Addie; (2) American Olivine Company with mines at Ellijay #9 (Stewart), Moor's Knob and the Fields Tract near Addie, and a processing plant at Dillsboro; (3) Spruce Pine Olivine Company with a mine and mill at Hinson Creek. Approximately

150,000 tons of processed olivine were sold in 1978 in North Carolina, and at least double that tonnage was mined as raw ore and overburden. These tonnages present a healthy growth when considering that in 1970 only about 30,000 tons of olivine products were sold in North Carolina and in 1960 not more than 10,000 tons were sold.

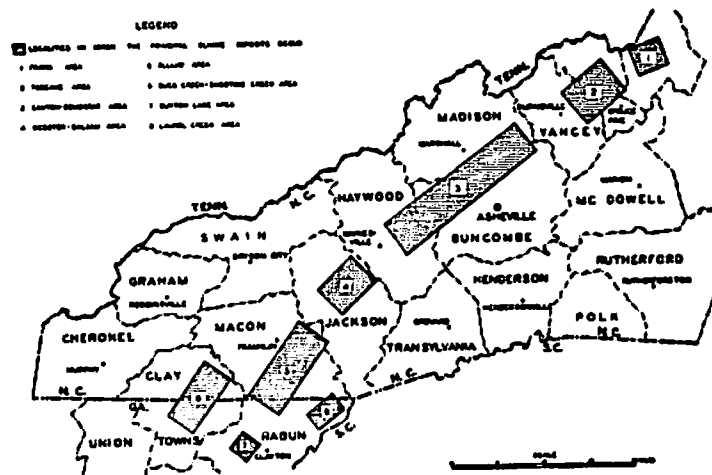


Fig. 3. Distribution of Olivine in the Tennessee Valley Area of Western North Carolina and Northeast Georgia (After Hunter, ref. 5). Olivine employed in this study came from Area 5; the specific deposit is identified as Ellijay #9 (Stewart).

North Carolina State University, through its Minerals Research Laboratory (Asheville) and the Engineering Research Services Division (Raleigh), has worked with industrial and mining interests to increase the use of olivine through applied research. In 1938, Greaves-Walker and Jones (ref. 6) studied the production of unfired and fired forsterite refractories from North Carolina dunites. In 1955, Banks and Wells (ref. 7) studied the beneficiation of olivine for foundry sands by means of a Humphrey Spiral, and in 1959, olivine uses and beneficiation methods were summarized by Wells (ref. 8). In 1972, Lewis (ref. 9) compared olivine flotation beneficiation techniques, and in the same year, beneficiation of olivine for foundry sand by calcining was studied by Redeker (ref.10).

Through the years, different olivine mining companies have employed the services of the Minerals Research Laboratory for property evaluation and process research and assistance with in-plant problems.

On a visit to olivine mining operations in Norway, Sweden and Austria in 1973, Redeker (ref. 11) studied the practice of the olivine industry in Europe and was impressed by the large tonnages of olivine consumed by the steel industry as flux in blast furnaces (olivine is used to control alkali buildup and for slag fluidity control; it seems to decrease energy requirements by up to 10% through increase in product through-put). The use of olivine as a flux in the steel industry has now become more common in the USA and has accounted for a large increase in olivine production in North Carolina (ref. 4, 12, 13).

Redeker (ref. 11) also observed that large tonnages of European olivine were being used (1973) as raw material for special manufactured ceramic cores used in electric heat storage units in areas where lower off-peak power rates were offered to level electric power plant loads, especially in Germany, England and France. Since that time, the University has initiated several studies under internal and external funding to promote the use of North Carolina olivine for energy storage. For example, samples from three different olivine deposits and from different stages of processing were sent to Dynamidon-Koppers in Dusseldorf, W. Germany to produce experimental core units for the German-made Stiebel-Eltron ETS heat storage units which are marketed in the USA by H. B. Electric Company in Rutland, Vt. (in that area of the northeastern US, heat storage is encouraged by Central Vermont Public Service Corporation's reduced off-peak electric rates). A 4 KW Stiebel-Eltron heat storage unit (single room space heater) was charged with experimental cores made in Germany from North Carolina olivine and demonstrated at the NCSU School of Engineering Energy Dome at the October, 1978 North Carolina State Fair. Also demonstrated there was a 30 KW central heat storage unit based on English technology under license from J. Hewitt & Son, and made in the USA by TPI Corp., Johnson City, Tennessee. For that demonstration, the central heat storage unit was charged with core units made in England from Norwegian olivine, but research was even then underway in the Engineering Research Services Division to fabricate similar shapes made from North Carolina olivine for evaluation in the TPI heat storage furnace. This paper is primarily concerned with results obtained to date in that ongoing study.

EXPERIMENTAL

Materials selections

In European heat storage furnaces, the practice has been to employ refractory ceramic shapes ("stones" or "bricks") based either upon magnesite (Germany) or upon olivine (England, Germany). Economics enter heavily into materials selections

for this application: magnesite bricks are denser and have better overall heat capacity (by up to 20%), but are much more expensive than olivine bricks. Magnesite appears to be the material of choice for very compact space heaters (1-10 kw range), but in larger units, where volumetric heat capacity per se is less critical an issue, the lower raw materials and fabrication costs for olivine bricks appear to give olivine the advantage. At this time, magnesite is considered too expensive for serious consideration in U.S. central system heat storage furnaces.

Laboratory experiments initiated by the University in January, 1979 were undertaken to provide an advance data base of chemical and physical analyses for foreign and domestic olivine raw materials and for existing olivine (and magnesite) heat storage bricks used in Europe. Sets of olivine refractory specimens (typically 114 x 57 x 25 mm) were also fabricated and fired, using various bond materials in combination with two olivine ores from different geographical locations within the North Carolina olivine belt. Pertinent data extracted from these preliminary studies were available to form a basis for scale-up activities when the present program began in June, 1978.

Table I gives typical chemical compositions of German and English olivine heat storage products, together with that of the parent Norwegian (or Swedish) olivine ores. For comparison, the table also includes a representative North Carolina olivine ore and laboratory specimens made from it. Table II summarizes densities and thermal properties of typical German and English olivine products, and for comparison, those of some of the initial compositions developed from North Carolina olivine in preliminary studies (early 1978) at N. C. State University.

When plotted on the triaxial MgO-FeO-SiO₂ phase diagram (ref. 14, not illustrated), all these olivine ores, and products derived from them, lie within a relatively small region in the forsterite-fayalite (olivine) solid solution field. With the possible exception of the alumina-modified, silica-rich English olivine brick product, compositions tend to fall along a line which is slightly more siliceous than, but approximately parallels, the forsterite-fayalite join.

If minor constituents are for the moment disregarded, the phase diagram shows these compositions to be rather refractory, having equilibrium liquidus temperatures (melting points) in the range 1800-1850°C (3272-3362°F). It also shows the adjacent (most probable) phases to be (1) on the silica-rich side, the less-refractory pyroxenes, notably enstatite, MgO·SiO₂, a common accessory mineral in olivine, and (2), on the magnesia- and/or iron oxide-rich side, a magnesiowüstite solid solution, (Mg, Fe_{1-y})O. The refractoriness of magnesiowüstite (and to a degree, that of olivine as well) depends not only upon a particular MgO-FeO-SiO₂ ratio (i.e., cation composition) but also upon oxygen partial pressure (i.e., cation-anion ratio, ref. 15). For a given cation composition, the lower P_{O₂}, the more

TABLE I
Chemical analyses of European and North Carolina olivines and of various heat storage bricks

	Typical Swedish Olivine	Typical Norwegian Olivine	Typical North Carolina Olivine	Typical German Olivine Brick†	Typical English Olivine Brick†	Shale-Bonded North Carolina Olivinet	Kaolin-Bonded North Carolina Olivinet
MgO	42.6 %	46.0 %	46.0 %	51.0	45.0	46.6	46.6
SiO ₂	41.5	43.4	42.8	41.0	41.5	42.9	43.0
Al ₂ O ₃	1.02	1.07	0.68	0.64	3.04	1.32	1.33
Fe ₂ O ₃	9.1	6.4	8.2	7.0	8.1	8.6	8.6
CaO	0.57	0.29	0.12	0.17	0.52	0.36	0.36
K ₂ O	--	--	0.04*	0.02	0.29	0.09	0.02
Na ₂ O	--	--	--	0.05	0.13	0.09	0.07
NiO	0.24	0.27	0.16	0.23	--	--	--
Cr ₂ O ₃	0.87	0.60	0.27	0.15	--	--	--
LOI	3.68	1.21	1.91	0.21	0.70	0.46	0.28

* Includes Na₂O

† Presumed to be made from Norwegian olivine

† Olivine from North Carolina's Ellijay #9 (Stewart) deposit.

reduced will be the Fe ions and the lower will be the resultant liquidus (and/or solidus) temperature.

From other phase diagrams (ref. 16), it is also evident that olivine-based ceramics will be relatively intolerant of alumina additives if refractoriness is to be maintained. Preliminary firing studies confirmed this point, and led to establishment of a practical upper limit of about 2.5% Al₂O₃ content for this investigation.

The German olivine brick subjected to analysis appeared to contain more MgO (and less Al₂O₃) than did the parent Norwegian ore; it presumably had been made somewhat more refractory by incorporating some magnesia-rich additive. On the other hand, the English olivine brick studied appeared to contain less MgO, but to be richer in Al₂O₃ (probably also in Fe₂O₃, and in RO and R₂O flux oxides) than the parent ore; presumably it had been rendered less refractory and more workable by an admixture of relatively impure (but probably quite plastic) clay or shale. A variety of x-ray, microstructural and physical evidences suggested that the German olivine product had been fired at much higher temperature than its English counterpart (ΔT ~260°-315°C, ~500°-600°F).

TABLE II
Preliminary comparisons of densities and thermal properties for European and (experimental) North Carolina olivine heat storage bricks

	Typical German Olivine Brick	Typical English Olivine Brick	Shale-Bonded N.C. Olivine Brick	Kaolin-Bonded N.C. Olivine Brick	
Bulk density, g/cm ³	2.68	2.57	2.56	2.69	
Pycnometric density, g/cm ³	3.29	3.20	3.25	3.29	
Fractional density	0.915	0.802	0.788	0.818	
Volumetric heat capacity, cal/cm ³ /°K	@ 100°C	0.607	0.568	0.562	0.609
	250°C	0.664	0.626	0.619	0.674
	400°C	0.631	0.651	0.615	0.688
	550°C	0.627	0.660	0.610	0.682
Thermal conductivity cal.cm/sec.cm ² °K x 10 ³	@ 100°C	4.76	4.31	5.12	5.03
	250°C	4.17	4.30	4.92	4.29
	400°C	3.49	4.15	4.30	3.52
	550°C	3.05	3.96	4.03	3.06

Based upon the foregoing analyses and results of the initial fabrication and firing studies, two different compositions (and firing regimes) were developed for use with North Carolina's Ellijay #9 (Stewart) olivine. In the first, maturing at -1370°-1400°C (-2500-2550°F), 2.5% plastic Georgia kaolin was added to facilitate fabrication and to establish a high temperature bond. In the second, maturing at -1205°-1232°C (-2200-2250°F), 5.0% North Carolina triassic shale was added. In each case, minus 9 mesh olivine grain was sized (in coarse, medium and fine fractions), blended in predetermined portions with the additive clay phase and -4% H₂O, then pressed, dried and fired to obtain final fractional densities in the 0.75-0.82 range, depending upon process parameters. X-ray crystallographic studies showed the principal phases present in the fired bodies to be (1) forsterite solid solution and (2) enstatite-like pyroxene(s).

Experimental procedures

In general, conventional research methods which require little comment have been employed in processing and characterizing the materials and products examined in this study. In brief, they included:

Composition. Wet chemical analyses for olivine ores, products, et al were carried out at the Minerals Research Laboratory, Asheville.* The results were

*Under the direction of Philip N. Sales.

found to be in very good agreement with those obtained for similar specimens by other interested investigators in the U.S. and Europe.

Density. Bulk density was determined by gravimetric means, using Archimedes principle. Small specimens were saturated with distilled H_2O in vacuo; some larger specimens were saturated by boiling and cooling in distilled H_2O . In lieu of a calculated theoretical density, the apparent specific gravity (pycnometric density) was determined for crushed (minus 80-mesh) material in N_2 with a Beckman air comparison pycnometer. Fractional density was calculated by dividing bulk density by the air pycnometric density.

Microstructure. Thin sections of olivine (dunite) ores and of fired products were prepared and examined by petrographic (optical) microscopy by the University's Department of Geosciences.* Fractographic specimens were examined by scanning electron microscopy (SEM), using a JEOLCO JSM-II instrument equipped with an EDAX nondispersive x-ray analyser. Quantitative electron beam microprobe line scans of selected, polished specimens were also carried out with a Philips Microanalyser.+

Thermal properties. Using specimens supplied by North Carolina State University, investigators at Virginia Polytechnic Institute and State University, Blacksburg, determined temperature-dependent thermal diffusivities and specific heats, respectively, for various olivine heat storage brick formulations and a magnesite brick reference specimen. The thermal diffusivity studies were carried out by laser flash technique** using cut and ground discs taken from fired bricks. Data were taken over the experimental range 25-1050°C. The specific heat experiments were carried out by differential scanning calorimetry++ over the temperature range 20-600°C, using powdered samples taken from the same fired blocks. The coefficient of thermal conductivity, K, was calculated as the product of (1) thermal diffusivity, (2) specific heat and (3) bulk density. Similarly the volumetric heat capacity, $cal/cm^3/°K$, was calculated as the product of (1) specific heat and (2) bulk density.

Processing full sized bricks. The large size and weight (~7.75 kg) of the English-designed olivine brick created some special handling problems in a laboratory primarily equipped for smaller specimens. For example, the only press available having adequate load capacity also had a very short stroke (<45 mm), so that pressing had to be done in three stages, using a succession of shim blocks to achieve the total stroke required. Because bottom stroke ejection was also precluded, it was necessary to remove and disassemble the die each time to release the formed piece. The specially shaped, hardened steel die weighed

*Under the direction of Professor Henry S. Brown.

+Under the direction of Ingeborg K. Simonsen.

**Under the direction of Professor D. P. H. Hasselmann

++Under the direction of Professor James P. Wightman

~160 kg, but had been designed and fabricated with these unusual requirements in mind. Even so, a strong, hard-working three man crew was required to handle the forming operations!

Batching and mixing was carried out on a one-brick-at-a-time basis using a small Hobart blender (see Table III). The prepared mix was double sealed in plastic bags to prevent loss of H₂O prior to use; the prepared mix could be stored up to ~72 hr.

The prepared mix was hand loaded, leveled and lightly tamped in the assembled and lubricated* die, the top punch was inserted, and the die bolts were tightened securely. After placing the filled die in the press, pressing proceeded in three stages, using shim blocks, until the final load, ~1.045 MN (~235,000 lb.), was reached and held for 1 min; the forming pressure was 30.0 MPa (~4350 psi). After removal from the press, the top punch was extracted, the bolts loosened, and the die was rotated 90° onto its side. One side plate, one end plate and the bottom punch were removed to expose the fabricated piece, which could then be carefully transferred to a small wooden pallet for air drying. After air drying for > 24 hours, the bricks were dried in a cabinet drier at 95-100°C for an additional 24-36 hr.

Firing was carried out in an available propane-fueled updraft periodic kiln designed and built by University personnel. Ware was open set, usually 12 bricks at a time, with 90% magnesite grain as a parting layer, on silicon carbide post-and-plate kiln furniture placed well above the inlet plane of the burners. Firings proceeded at ~120°C/hr. (~250°F/hr.) to ~650°C (~1200°F), and at ~177°C/hr. (~350°F/hr.) to maturing temperature. Shale-bonded brick were fired to cone 6-7 at ~1204°C (~2200°F). Kaolin-bonded brick were fired to cone 14 at ~1371°C (2500°F). In each case, soak time was 3 hr. at the maturing temperature. Though test firings at cone 14 had shown minimal (< 1/4 cone) variation across the open kiln setting space, a consistent pattern of slight overfiring was observed for kaolin-bonded bricks which had been placed in the left portion of the kiln. This effect is tentatively attributed either to local variations in velocities of the combustion gases, or to similar flow-related variations in local redox conditions. Kaolin-bonded bricks could not be fired reliably at cone 14 in upright or in double-stacked configurations because of creep distortions. At cone 6-7, shale-bonded bricks were fired successfully in upright as well as horizontal orientations, but were subject to some creep distortion when double stacked. However, access to a conventional forming press would be likely to permit more effective compaction (higher green density) during fabrication, thereby making it possible to reduce the maturing temperature required to yield a given final

* Isostearic acid, lightly wiped over die surfaces.

fractional density, thus avoiding (or at least minimizing) incipient creep problems during firing.

TABLE III
Batch compositions for experimental full sized olivine brick

Constituent	Shale-bonded (cone 6-7)		Kaolin-bonded (cone 14)	
	grams	(%)	grams	(%)
Ellijay #9 olivine:				
coarse (-8, +20 mesh)	3013	(39.03)	3013	(39.03)
medium (-20, +65 mesh)	2259.5	(29.27)	2259.5	(29.27)
Fine (-65 mesh)	2071.3	(26.83)	2259.5	(29.27)
Subtotal, olivine	7343.8	(95.12)	7532.0	(97.56)
Bond phase:				
triassic shale (-100 mesh)	376.4	(4.876)		
kaolin (Ajax P)			189.2	(2.44)
Subtotal, ceramic solids	7720.2	(100.0)	7720.2	(100.0)
Organic additives				
methyl cellulose binder	21.03	(0.272)	21.03	(0.272)
Additive A	1.04	(0.014)	1.04	(0.014)
Water	300.6	(3.89)	300.6	(3.89)
Totals	8042.87	(104.27)	8042.87	(104.27)

RESULTS AND DISCUSSION

Materials selections

The Ellijay #9 (Stewart) olivine ore selected for use in this demonstration study displays good performance in ceramics. It is appropriate to note that not all North Carolina olivines are alike; rather, they tend to vary considerably in the degree of initial serpentinization, in the makeup of accessory minerals, and in the degree of subsequent weathering. Though the primary olivine phase continues to make up the bulk of the ceramic when fired, it is the accessory minerals, including those deliberately introduced as mill additions, which tend to dominate the firing behavior and to exert a very strong influence upon the character of the interfacial bonding between the relatively coarse, rather inert grains of the refractory olivine (see Fig. 4).

On the basis of limited experience gained in preliminary studies here and elsewhere involving five or more different deposits from the N.C. olivine belt, each of which had had little or no beneficiation, it is possible to predict good to excellent ceramic performance for those olivine ores like Ellijay #9 which display (1) relatively low concentrations of R_2O and RO flux oxides, (2) low ignition losses and (3) relatively high $MgO:SiO_2$ ratios. Of the five materials studied, two appear to have ceramic potential equal to or better than the

Ellijay #9 (Stewart) deposit reported here, while two others appeared to be inferior in the same regard. It remains to be shown whether or not appropriate combinations of (1) mineral beneficiation before ceramic processing and/or (2) adjustments of the accessory mineral makeup by means of appropriate mill additions and firing conditions during ceramic processing, can ultimately be employed to make the ceramic performance of olivine refractory products less sensitive to these natural variations from deposit to deposit.

Processing of full sized bricks

More than 100 full sized bricks (see Fig. 2a) were successfully fabricated

TABLE IV

Dimensions, weights, densities and properties of full sized English-made and University-made olivine bricks for testing in 30 kw TPI heat storage furnace.

	Reference English olivine brick	NCSU olivine brick, kaolin-bonded*	NCSU olivine brick, shale-bonded*
Dimensions, mm			
length	~247.0	~247.1	~247.6
width	~166.6	~164.5	~165.1
height	~ 86.3	86.3 ⁺¹ ₋₂	90.03 ^{+0.6} _{-0.3}
Weights, kg			
green	---	7.81 ^{+0.15} _{-0.06}	7.82 ^{+0.08} _{-0.03}
dried	---	7.73 ^{+0.16} _{-0.06}	7.69 ±0.03
fired	~ 7.51	7.57 ^{+0.15} _{-0.16}	7.58 ^{+0.03} _{-0.01}
Compressive Strength, 25°C, MPa	~10.75	~13.16	~7.38
Densities			
bulk, g/cm ³	2.57	2.58	2.41
pycnometric, g/cm ³	3.20	3.29	3.25
fractional	0.802	0.783	0.742
Volumetric Heat Capacity cal/cm ³ °K	@ 100°C 0.569 250°C 0.626 400°C 0.651 550°C 0.660	0.571 0.632 0.645 0.639	0.524 0.576 0.572 0.570
Thermal Conductivity $\frac{\text{cal cm}}{\text{sec cm}^2 \text{°K}} \times 10^3$	@ 100°C 4.31 250°C 4.30 400°C 4.15 550°C 3.96	6.16 (6.96) ⁺ 4.55 (5.94) 3.09 (4.77) 2.56 (4.16)	5.45 5.19 4.35 3.65

*Dimensions and weights are given as means and extremes for a typical lot of 12 units.
+Values shown are for heat-up, those in parentheses are for cool-down; the apparent hysteresis in thermal conductivity is tentatively attributed to effects of microcracks on thermal diffusivity (ref. 17).

and fired during the present project (Table IV). Approximately 50% of the finished units were shale-bonded, the balance were kaolin-bonded.

The decision to proceed with fabrication of both bond types was based on preliminary studies (see Table II). It took into account (1) the relative ease of processing, the lower firing temperature and the projected lower manufacturing costs of the shale-bonded olivine product, and (2) the higher density, higher volumetric heat capacity and better overall bond strength and "finish" of the higher-fired (and probably more expensive) kaolin-bonded brick. Further, the available thermal property data for the two materials suggested the possibility of temperature-dependent crossovers between the pertinent thermal properties (volumetric heat capacity determines how much heat can be stored in a fixed-volume ceramic heat reservoir at given temperatures, whereas the coefficient of thermal conductivity determines in large part how rapidly heat can be safely stored up at given temperatures during the charge cycle, and how effectively it can again be extracted during the discharge cycle, and particularly so near the low temperature end of the cycle).

On the one hand, the kaolin-bonded preliminary specimens displayed favorably high volumetric heat capacities at high temperatures, however (possibly because of pre-existing and/or induced microcracks, see Fig. 4c and ref. 17, its thermal conductivity was high in the low temperature regime, but relatively low at high temperatures. By comparison, the shale-bonded specimens displayed lower but less temperature-dependent values for volumetric heat capacity, yet had higher values for thermal conductivity, also somewhat less temperature-dependent. These findings are in good agreement with the liquid-assisted, well sintered grain-to-grain bond structure of the former, and with the rather glassy second phase bonding of the latter. They also show clearly that engineering trade offs between thermal properties for such an application will be quite sensitive to materials selections, and in all probability, to materials processing parameters as well. The important role of these interrelated ceramic materials-processing factors in optimizing the overall thermal performance of a given heat storage system should be obvious to ceramists, and perhaps to heat storage furnace designers as well.

As an example, the thermal properties data of Table II for NCSU-formulated blocks had initially been obtained on materials pressed at 55.16 MPa (~8000 psi), whereas later, for several practical reasons, it had only been possible to press full sized bricks (data of Table IV) at 30 MPa (~4350 psi). Bulk densities and thermal properties of the full size bricks (Table IV) were therefore lower than those of the original small test blocks (Table II). Since both thermal properties of interest depend linearly upon bulk density, it should be possible to compare them on a normalized density basis. To achieve such a normalization at the original small block density value, the kaolin-bonded full size brick would be

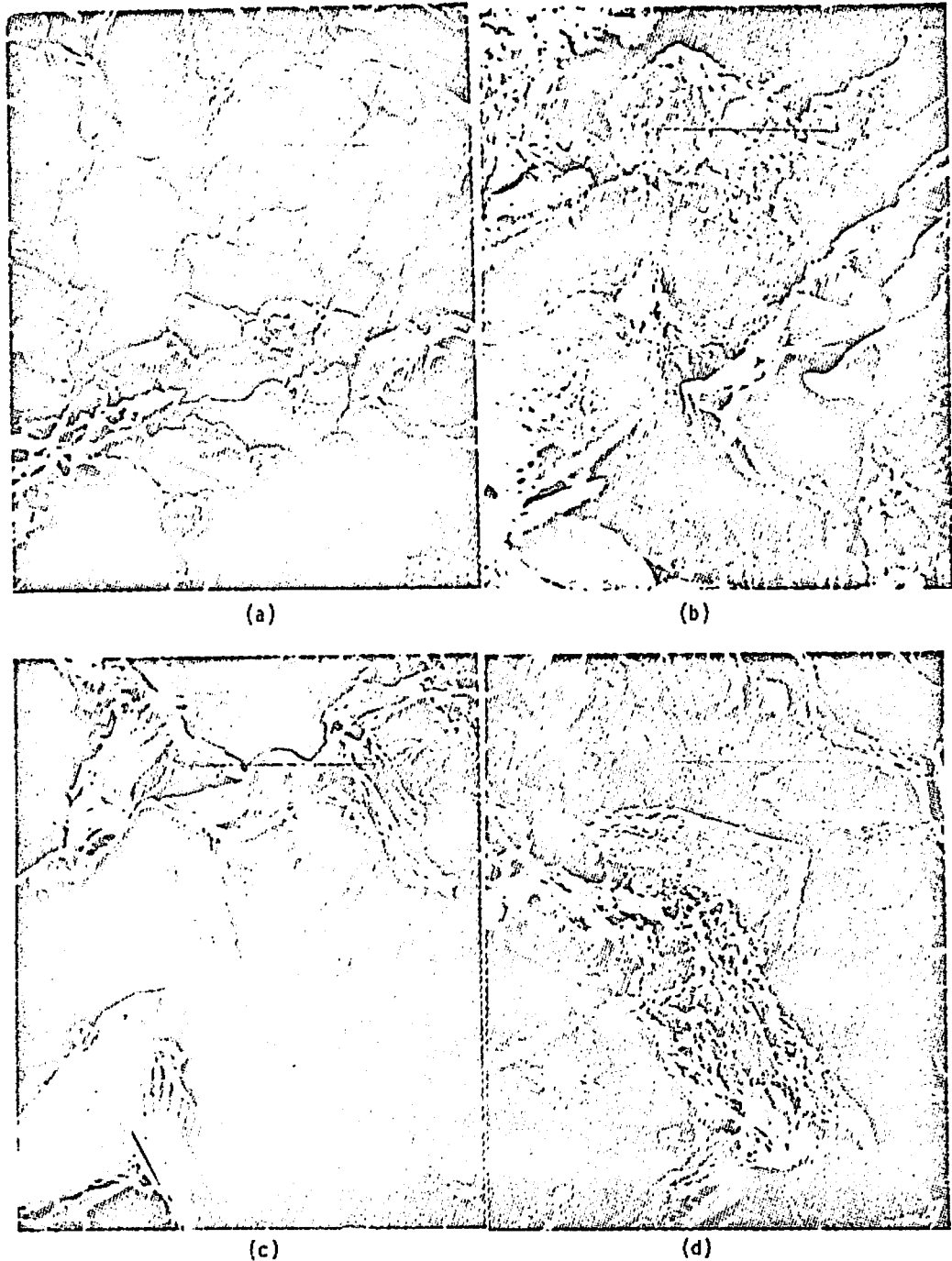


Fig. 4. Microstructural features of various olivine heat storage refractories: (a) typical German brick, (b) typical English brick, (c) kaolin-bonded NCSU brick, (d) shale-bonded NCSU brick. SEM fractographs, X180.

increased by ~4.26%, and the shale-bonded brick by ~6.22%. For volumetric heat capacity, this simple normalization resulted in good predictability: over the range of temperatures involved, the predicted value for kaolin-bonded brick was high by ~0.015 cal/cm³/°K, and for shale-bonded, by ~0.008 cal/cm³/°K. Predictability was less good for thermal conductivity values, which tended to be high by as much as 0.5-0.9 $\frac{\text{cal. cm.}}{\text{sec. cm}^2 \text{°K}}$ x 10³. Though the compositions were nominally the same for small blocks and full size bricks, there were many minor differences (material lots, grain sizing, mixing procedures, et al.) in addition to forming pressure per se which could readily account for variations of this magnitude.

For a given starting material, better ceramic processing (as embodied in higher forming pressures, better material preparation, etc.) clearly does offer an important route (by means of higher bulk densities) to direct improvements in heat storage capacity. However, these improvements may not be entirely penalty-free: higher fractional densities also carry with them a concomitant risk of increased vulnerability to thermal shock failure. Apparently, little information is currently available to permit direct analytical assessment of thermal stress factors in heat storage applications. Under the circumstances, it would be prudent to limit the fractional density to a safe level in the range 0.825-0.850 until actual thermal shock conditions can be better evaluated (see Demonstration and Evaluation, below).

In normalizing the thermal properties at such an upper limit value of fractional density (arbitrarily, 0.825), it would be necessary to increase the bulk density of the English brick by ~2.7%, of the NCSU kaolin-bonded brick by ~5.2%, and of the NCSU shale-bonded brick by ~11.3% (improvements of that magnitude are considered to be well within the scope of the ceramic processor's art). For such a normalization, one would predict relative thermal properties shown in Table V.

DEMONSTRATION AND EVALUATION

The data of Tables IV and V indicate that full sized bricks of N.C. olivine should perform about as well as, and possibly better than, the English-made equivalents in heat storage furnace applications. To demonstrate this point, and to provide opportunities to reexamine specimens after repeated diurnal cycling within the core of the heat storage furnace, arrangements were made with the manufacturer, TPI, Inc., to obtain a 30 kw industrial heat storage unit* for demonstration and evaluation studies in the University laboratory.

* Off-PeakTM Comfort Conditioning Storage Equipment, Model 21530, rated 30 kw @ 240 v, 1φ, 60 Hz, 120.3a. With the manufacturer's assistance, the unit was internally rewired to operate on an available 208 V, 3φ, 60 Hz, 60a circuit.

TABLE V

Predicted thermal properties for various heat storage bricks at uniform fractional density.

		English olivine brick	NCSU olivine brick, kaolin-bonded	NCSU olivine brick, shale-bonded
Fractional Density		0.825	0.825	0.825
Bulk Density, g/cm ³		2.64	2.71	2.68
Volumetric Heat Capacity	@ 100°C°	0.584	0.600	0.583
	250°C	0.643	0.664	0.641
	400°C	0.688	0.678	0.636
	550°C	0.671	0.672	0.634
Thermal Conductivity				
	@ 100°C	4.428	6.480 (7.322)*	6.063
	250°C	4.418	4.797 (6.248)	5.763
	400°C	4.264	3.250 (4.534)	4.480
	550°C	4.068	2.693 (4.376)	4.060

* Use open values for heating, those in parentheses for cooling.

For the initial full scale demonstration with N.C. olivine bricks, now in progress, the 144 unit core (12 layers, 12 bricks per layer) was divided in four separate vertical quadrants (1 x 3 x 12 units per quadrant). English bricks were used to form two diagonally opposite quadrants, N.C.S.U. kaolin-bonded brick in one, and N.C.S.U. shale-bonded bricks in the other of the two remaining quadrants. A total of 24 open tipped, Inconel sheathed, chromel-alumel thermocouples, reading on a multipoint strip chart recorder, were installed in selected locations within the core to monitor (1) heating element - brick interface temperatures, (2) center-of-brick temperatures, and (3) air channel temperatures for each type of material (see Fig. 5).

This important phase of the overall study is proceeding well, with fairly strong indications that the actual performance data will be found to be generally in agreement with expectations from the data of Table IV. Final results of this ongoing phase of the present study will be reported elsewhere at a later time.

ACKNOWLEDGEMENTS

Support by the State of North Carolina through its North Carolina Energy Institute, and by the University's Engineering Research Services Division and its Minerals Research Laboratory, is gratefully acknowledged. American Olivine Company, Dillsboro, N. C., generously provided raw materials. TPI, Inc., Johnson City, Tenn., provided a full scale heat storage furnace and stocks of English-made brick, as well as much valuable technical information. Ron Cochrane served as project ceramic engineer and was ably assisted by his fellow ERSD staff members, Michael Paisley and Geoffrey McGaughey. Their physical efforts, their personal enthusiasms and their many clever ideas have made invaluable contributions to the whole study.

English bricks:

left front quadrant
back right quadrant

NCSU kaolin-bonded bricks:

back left quadrant

NCSU shale-bonded bricks:

right front quadrant

Thermocouples project
outwards from front face.

Front face insulation,
terminal strip for heating
elements (center front)
and outer front panels not
yet installed.

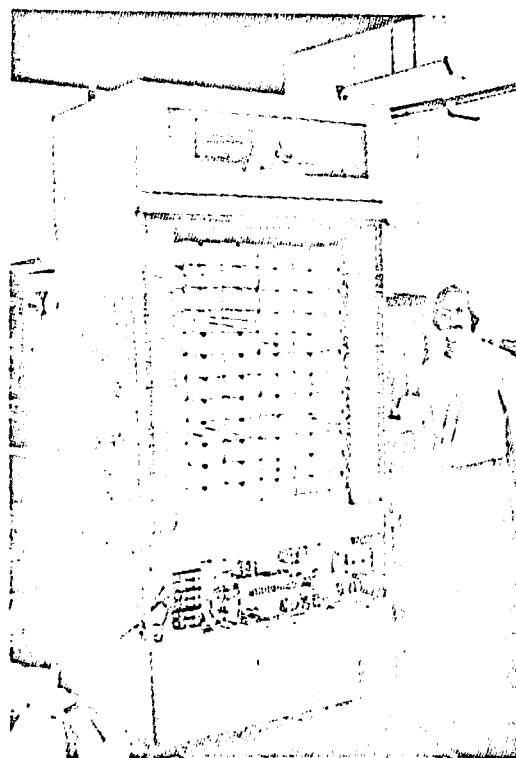


Fig. 5. Assembled, instrumented olivine brick core in place in TPI, Inc., 30 kw Off-PeakTM Heat Storage Furnace.

REFERENCES

- 1 K. Beckius, "Olivine: Its Properties and Uses," *Industrial Minerals*, Feb., 1970.
- 2 H. Bjoerum, "Olivine: An Interesting Industrial Mineral," *Industrial Minerals*, Dec. 1975.
- 3 "Opportunities for Increasing Olivine Output," *Industrial Minerals*, Feb., 1970.
- 4 "Olivine and Dunite Blast Furnace Usage Adds New Dimension," *Industrial Minerals*, May, 1977.
- 5 C.E. Hunter, Forsterite Olivine Deposits for North Carolina and Georgia. Bull. No. 41, Dept. of Conservation and Development, Raleigh, N. C., 1941.
- 6 A.F. Greaves-Walker and R.L. Stone, The Production of Unfired and Fired Forsterite Refractories from North Carolina Dunites. Bull. No. 16, Engr. Expt. Sta., State College Station, N. C., 1938.
- 7 M.K. Banks and W.G. Wells, Beneficiation of Olivine by Means of a Humphreys Spiral. Industrial Information Series, Bull. No. 10, Department of Engineering Research, N. C. State College, Raleigh, N. C., 1955.
- 8 W.G. Wells, Olivine Uses and Beneficiation Methods. NCSU Minerals Research Laboratory Bull., Vol. 1, No. 2, 1959.
- 9 R.M. Lewis, Comparison of Olivine Beneficiation Techniques, NCSU Minerals Research Laboratory Rept. No. 1, 1972.
- 10 I.H. Redeker, Beneficiation of Olivine for Foundry Sand by Calcining. NCSU Minerals Research Laboratory Rept. No. 2, 1972.
- 11 I.H. Redeker, "Olivine and Feldspar Mining in Europe," presented at meeting of the Carolinas Section of AIME, Charleston, S. C., March 8-9, 1974.

- 12 International Minerals Corp., Annual Report, 1977
- 13 Ross, R. E., Optimum cleaner practice to avoid slab formation and provide smooth blast furnace operation with low stability alkali-bearing coke. Youngstown Sheet and Tube Co., Indiana Harbor Works, East Chicago, Indiana, 1978.
- 14 E. M. Levin, C. R. Robbins and H. F. McMurdie, Phase Diagrams for Ceramists. The American Ceramic Society, Inc., 1964 Edition, Fig. 682, FeO-MgO-SiO₂, p.236.
- 15 A. Muan and E. F. Osborn, J. Am. Ceram. Soc. vol.39, 1956, pp.121-140.
- 16 In ref. 14:e.g., Fig.696, FeO-Al₂O₃-SiO₂,p.241.
- 17 D.P.H. Hasselmann, Analysis of thermal stress resistance of micro-cracked brittle ceramics. To be published.

Authors' note:

In mid-May, shortly before the convening of CIMTEC IV, it was announced that the North Carolina Utilities Commission had approved, and the privately owned utilities have offered, off-peak electric energy pricing policies for those residential, industrial and commercial customers meeting a predominant share of their space conditioning needs (heating or cooling) with energy storage devices such as the heat storage furnace discussed here. Details of differential rate structure(s) under the new off-peak policy are not available of time of writing.