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Dolomite Refractories, and Their Potential as Substitutes for Imported Chromite

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LIST OF UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu/ft^3	British thermal unit per cubic foot
°C	degree Celsius
g/cm^3	gram per cubic centimeter
hr	hour
lb	pound
min	minute
μm	micrometer
mm	millimeter
pct	percent
pct/min	percent per minute
psi	pound per square inch
wt-pct	weight-percent

DOLOMITE REFRACTORIES, AND THEIR POTENTIAL AS SUBSTITUTES FOR IMPORTED CHROMITE

By Timothy A. Clancy[1]

ABSTRACT

To help reduce the Nation's dependence on imported chromite, the Bureau of Mines is conducting research on the use of dolomites as an alternate material. Dolomite is a plentiful domestic resource and offers certain advantages as a refractory raw material. A review of the literature has indicated that there are many sources of high-purity dolomite in this country and that European nations use a greater proportion of dolomite refractories, primarily in steelmaking, than the United States. The Bureau of Mines characterized 14 domestic dolomites as to chemistry, density, mineralogy, microstructure, and thermal behavior, to develop baseline data on their suitability as refractory raw materials.

INTRODUCTION

To help ensure a dependable domestic supply of essential minerals, the Bureau of Mines initiated an evaluation of domestic dolomites as a refractory raw material. Increased use of domestic dolomite as a refractory material would lessen the Nation's dependence on imported chromite and high energy consuming materials, such as seawater periclase. Historically, (10)[2] the United Kingdom, West Germany, Austria, and Japan have developed greater use of dolomite refractories than the United States particularly in secondary refining processes for steelmaking. In 1979, Western Europe used 28.6 lb of dolomite refractories per ton of steel produced versus 14.8 lb of dolomite refractories for the United States.

This paper reviews the properties and uses of dolomite refractories. Some preliminary data on the chemical and physical properties for 14 different raw domestic dolomite ores are included. These data will be used in future studies for comparison with the refractory properties of calcined grain produced from these ores.

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

DOLOMITE ORE

ORIGIN AND MINERALOGY

Dolomite (3) ($CaCO_3 \cdot MgCO_3$), identified by Dolomieu in 1791, occurs as sedimentary deposits similar in nature to limestone. Geologically some dolomites are precipitated directly from seawater but most dolomites are a result of the alteration of calcium carbonate sediments or rocks by hypersaline brines. Good examples are the almost-pure dolomite Silurian reefs in northern Illinois, Indiana, and Ohio, and in southern Michigan. Other carbonate minerals are found associated with dolomite, but usually not in great quantities.

Because of their similar physical properties, it is not easy to distinguish one carbonate mineral from another. The rate of solubility of the different minerals in dilute hydrochloric acid is the best technique to identify them in the field. Calcite is much more soluble in dilute acid than dolomite, so if a fresh rock surface is etched, the amount of dolomite left in relief can be estimated visually. X-ray diffraction is commonly used in the laboratory for determining carbonate mineralogy of bulk samples. Thin section petrographic analysis may be helpful, although it is difficult to distinguish carbonates in thin section unless staining techniques are used.

Impurities in dolomites vary considerably, but are economically important only if they affect the end uses of the rock. Impurities are tolerable for some uses if disseminated uniformly throughout the rock. Probably the most common impurity in dolomites is clay. The clay minerals, mainly kaolinite, illite, chlorite, smectite, and mixed lattice types, may be either evenly distributed or concentrated in laminae or thin partings. Chert, another common impurity, may be disseminated, or concentrated in nodules, lenses, or beds. It is composed mainly of very fine quartz (SiO_2) that easily incorporates impurities into its structure so it may be found in almost all colors. Silica is also found in dolomites as discrete silt or sand-size grains of quartz.

Dolomite and other carbonates are normally classified as to composition. High-calcium limestone is more than 95 pct $CaCO_3$, high-purity carbonate rock is more than 95 pct combined $CaCO_3$ and $MgCO_3$, and high-magnesium dolomite is more than 43 pct $MgCO_3$ (theoretically pure dolomite is 45.7 pct $MgCO_3$). The mineralogical properties of dolomite are given in table 1.

TABLE 1. - Mineralogical properties of dolomite

Crystal system......	Hexagonal.
Moh's hardness......	3.5 to 4.0.
Specific gravity....	2.87
Color...............	White or pink.
Refractive indices:	
ε................	1.500
ω................	1.679
Birefringence, δ....	0.179
Solubility..........	Slightly soluble in cold dilute HCl.

REFRACTORY GRADE DOLOMITE

The American Society for Testing and Materials (1) classifies dolomite refractory raw materials as (1) raw refractory dolomite, (2) calcined refractory dolomite, and (3) dead-burned refractory dolomite. This classification is based primarily on MgO content, loss on ignition, and impurity contents. Table 2 lists the requirements for each of these classes of refractory dolomite.

TABLE 2. - Classification of granular refractory dolomite (ASTM C468-70), weight-percent

Classes	MgO content, minimum	Loss on ignition, maximum	Impurities, maximum			
			SiO_2	Al_2O_3 + TiO_2	Fe_2O_3 range	Sulfur
Raw refractory dolomite, "as received" basis	16	NAp	1.75	1.50	NAp	0.08
Calcined refractory dolomite, ignition-free basis	33	2.0	2.00	2.50	NAp	.16
Dead-burned refractory dolomite (rotary kiln-fired), ignition-free basis	32	2.0	2.25	2.50	4-10	NAp

NAp Not applicable.

The use of dolomite as a refractory appears to have started in about 1878 when S. G. Thomas experimented with tar-bonded dolomite linings in a Bessemer converter. Much of present-day dolomite refractory technology was developed in England during World War II. Since then, England has made great use of dolomite raw materials for refractories. Chesters (4), in a chapter devoted to dolomite, presents the compositions and properties of raw refractory grade dolomite. Some of the data are included in table 3. The compositions are similar to those for dolomites described by others (5, 26-27). However, besides compositional requirements the physical properties, such as grain density, refractoriness, strength, and microstructure, of a refractory dolomite material are important.

TABLE 3. - Composition and properties of refractory grade dolomites

Origin and formation	Chemical analysis, wt-pct					Physical properties		
	SiO_2	R_2O_3[1]	CaO	MgO	Loss on ignition	Specific gravity	Bulk density, g/cm^3	Porosity, pct
GREAT BRITAIN								
Dolomite (theoretical)	NAp	NAp	30.41	21.87	47.72	NAp	NAp	NAp
Lower Permian systems:								
South Yorks[2]	0.33	0.52	30.63	21.50	47.37	2.84	2.47	13.0
Derby	.74	.72	30.25	21.28	47.00	2.84	2.41	15.1
Notts	.87	.60	30.32	21.23	47.13	2.85	2.39	16.3
Durham: Permian system[3]	.89	.96	30.6	20.6	46.95	2.85	2.53	11.2
South Wales: Carboniferous limestone[4]	1.28	.81	32.48	19.41	45.15	2.82	2.77	1.8
UNITED STATES								
Ohio: Niagara system	.40	.80	30.1	21.0	47.20	2.87	2.66	7.9
	.02	.17	30.6	21.2	47.50	2.87	2.55	12.5
Pennsylvania: Ledger system	.30	.65	30.8	21.1	47.10	2.84	2.78	2.1
Missouri: Bonne Terre system	.31	3.73	31.16	19.2	45.44	2.84	2.68	6.0

NAp Not applicable.
[1] $R_2O_3 = Al_2O_3 + Fe_2O_3$.
[2] Soft.
[3] Medium to soft.
[4] Very hard.

The quantity of dolomite produced for refractory uses is not a large portion of the total U.S. dolomite production. More than three-fourths of the dolomite quarried in the United States is used as an aggregate or a soil conditioner. In 1980 (19), the production of refractory dolomite amounted to a total of 494,000 tons which was only 2.6 pct of the total lime and dolomite volume. The only States mentioned by Colby (5) as producing refractory grade dolomite were Alabama, California, Colorado, Illinois, Michigan, Nevada, Ohio, Pennsylvania, Utah, and West Virginia.

Ohio produces more dolomite than any other State and, in fact, produced approximately 55 pct of the dead-burned dolomite consumed in the United States in 1979 (9). While most of the major refractory companies in the United States produce their own raw materials for fire clay, high-alumina, and magnesia products, they have not developed the facilities to handle refractory dolomite. Dolomite materials are produced by five or six of the smaller companies.

Unpublished information by a leading dolomite producer (10) indicates that the use of dolomite as a refractory was not popular in the United States until recently. Since about 1912, dolomite in the United States has only been produced with iron added to make fettling grain. Although used extensively as a refractory in Europe from the time of the Bessemer converter (1860's), high-purity dolomite was essentially unavailable in the United States as a refractory raw material until the early 1960's when both Basic, Incorporated, and the J. E. Baker Co. began to produce a high-purity, high-density dolomitic grain. In Europe, on the other hand, very little fettling grain was produced and nearly all the dolomite was produced as a high-density, high-purity refractory raw material. The greater shortage and higher price of high-quality magnesite in Europe, as compared with the United States, probably contributed to the earlier development of refractory dolomite materials in Europe.

U.S. DOLOMITE DEPOSITS

Colby (5) in 1941 and Weitz (26) in 1942 published extensive surveys on the dolomite resources of the United States and described the quantity, quality, and uses of the deposits of each State. The States with the most plentiful deposits of dolomite are Ohio, Indiana, Illinois, Wisconsin, Michigan, and Pennsylvania. Individual deposits are reported with reserves varying from 10 to 350 million tons. Chemical analysis data are presented for 212 deposits in Ohio, 18 in Indiana, 27 in Illinois, 111 in Wisconsin, 76 in Michigan, and 102 in Pennsylvania. All of these deposits are considered to be high-grade dolomite materials that are defined by Weitz as material containing at least 98 pct total carbonates and less than 2 pct impurities including iron oxide, alumina, and silica.

Additional information concerning dolomite resources is available in State Geological Survey publications of California, Illinois, Indiana, Michigan, Virginia, West Virginia, and Wisconsin. The Alabama Geological Survey (25) reported that 11 dolomite quarries are in operation primarily in the Birmingham area. Total reserves of these quarries are estimated in billions of tons. Chemical analyses of these products indicated that most would be considered to be high-grade dolomites. The West Virginia Survey (27) provided information on limestone and dolomite quarries in that State. Only two of the quarries presently produce dolomite.

DOLOMITE REFRACTORIES

AGGREGATE PROCESSING

The original refractory use of dolomite was in the uncalcined condition in open hearths or Thomas converters. As steel processing became better controlled, the need for calcined dolomite grain increased. Chesters (4) provides a good summary of the processing of dead-burned dolomite or "doloma," as it is called in England. The production of doloma follows the reaction

$$MgCa(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad (1)$$

$$CaCO_3 + MgO + CO_2 \rightarrow CaO + MgO + 2CO_2. \qquad (2)$$

This decomposition process is commonly called calcination. Dolomite can be lightly calcined, as low temperature decomposition is called, or high fired to produce the dead-burned material. Production of higher purity dolomites, or low flux dolomites, has necessitated higher firing temperatures to produce dead-burned grain of satisfactory density.

In the temperature range of 600° to 900° C, the dissociation of dolomite results in the intermediate formation of calcium carbonate and magnesia, but heating above 900° C leaves only magnesia and lime as the products. On further heating, these oxides undergo crystal growth, the eventual size being very small in both cases. If reaction 2 is stopped immediately after the CO_2 is driven off, around 900° to 1,000° C, the product is too reactive and porous for use as a refractory raw material. Therefore, the calcination must be carried out at temperature of about 1,700° C in order to reduce the amount of porosity.

Very tight control is needed in the manufacture of calcined dolomite, as refractories produced from it can suffer from one or the other of the following:

1. Tendency to hydrate owing to reaction of free lime with moisture in the air.

2. Tendency for "dusting" or disintegration owing to an inversion and volume change on cooling of dicalcium silicate formed in the material.

The term "stabilization," as associated with dolomite refractories, has been used to cover the following three procedures:

1. The coating of calcined dolomite with pitch to reduce the rate of hydration.

2. The conversion of free lime to a silicate or ferrite to reduce hydration.

3. The addition of boric acid, phosphates, or other "stabilizers" to prevent the inversion of dicalcium silicate.

It would appear better to use the word "stabilization" solely for the last two procedures.

In a Bureau of Mines publication in 1942, Schallis (20) presented a survey on the calcination of raw dolomite. Particular mention is made of the hydration problem of dead-burned dolomite. Methods such as coating with tar or covering with treated paper have been successful in permitting storage for a few weeks or even a few months. To aid calcination, help stabilize the calcium oxide, and improve its ability to sinter, iron oxide was added to dead-burned dolomite before the charge went to the kiln. Also, it has been found that the conversion of the lime into dicalcium and tricalcium silicates by the addition of silica will reduce the hydration tendency of the lime.

Unfortunately, tricalcium silicate will break down into lime and beta dicalcium silicate, which is not volume stable and tends to disintegrate. In order to stabilize the dicalcium silicate, iron oxide can be added to the dolomite. Seil (21-23) received several patents directed toward stabilization of dead-burned dolomite grains by incorporating specified additions of SiO_2 and Al_2O_3 as a means of reducing hydration tendencies. Similarly, Lee (13) patented processes for the formation of low melting liquid phases in dolomite refractories in order to improve hydration resistance.

While the use of so-called "stabilized" dead-burned dolomite was extensive in the past, this practice is not in widespread use today. One reason for this fact is that the silica and iron oxide additions reduce the refractoriness of dolomite; another reason is that producers and consumers of dolomite materials have developed better handling methods for reducing hydration.

Most of the dolomite used for refractories is produced in either shaft kilns or rotary kilns. Both types are normally fired with gas or oil. Some European shaft kilns have been operated like blast furnaces, using alternating layers of raw dolomite and coal. Prior to firing, the dolomite is crushed and screened to a size suitable for feeding to the kiln. Material for feeding to shaft kilns is usually between 50 and 150 mm while materials for feeding to a rotary kiln is usually between 3 and 40 mm. In both cases, the crushed feed is washed with water to remove fine particles, particularly clay contaminations. The thermal processes can be considered as divided into the following four stages: drying; calcination, yielding a porous mixture of lime and magnesia; burning, in which porosity is greatly reduced; and cooling, which mainly serves to preheat incoming air.

Lee (14), in 1962, described a means to achieve higher firing temperatures and higher heating efficiencies by the use of insulating brick as a backup lining and the use of oxygen additions to the combustion air. An addition of high-purity oxygen comprising 3 to 10 pct of the total oxygen in the enriched combustion air is adequate to give the firing conditions necessary to produce dense grain.

A recent departure from this conventional single-stage firing process has been the introduction of a two-stage firing process involving a pelletization or high-pressure briquetting stage. This process is particularly useful for producing high-density grain from dolomites that are difficult to dead-burn to a high density in a single-stage process. The dolomite is first decomposed to produce a reactive oxide that is then pelletized and dead-burned in a rotary or shaft kiln to densities of 3.20 to 3.30 g/cm^3.

As described by Obst (17), it is also possible to produce magnesia-dolomite clinkers (coclinkers) by mixing the reactive oxide with reactive magnesium oxide before pelletization. These clinkers can have MgO contents from 50 to 80 pct. The amount of direct bonding between the periclase grains increases in proportion to the MgO content. Coclinkers has all the advantages and disadvantages of dolomite, but has a higher MgO content. It is preferred to achieve the MgO enrichment by addition of calcined MgO grains, especially in the fine fraction.

Chesters (4) compared the chemical compositions of British dolomites and those of other dead-burned materials. Results of this comparison are given in table 4. Present-day commercial dead-burned dolomite contains small amounts of silica, alumina, and iron oxide as accessory oxides. The iron oxide is usually present as the ferric form and will combine with lime to form dicalcium ferrite. Usually a small amount of iron will exist as FeO. The ratio of ferric to ferrous oxide will depend on the firing temperature and combustion conditions in the kiln. Alumina is not reduced under ordinary conditions and forms mineral phases that have low melting temperatures. Therefore, it is desirable to keep the alumina contents of dolomite refractories relatively low.

The overall chemistry as well as the ratio of accessory oxides to the combined MgO and CaO content affect both physical and chemical resistance of dead-burned dolomite grains. Since the majority of dolomite grains are used in the form of organically bonded brick or specialty mixes, this is the logical form in which to measure hydration resistance. Hubble (8) devised a hydration test that led to the establishment of a standard test, ASTM C492-66 (2). Dolomite material of a plus 35-mesh size was placed in a cabinet at a temperature of 71° C and relative

TABLE 4. - Typical properties of dead-burned dolomite grains

Origin	Chemical analysis, wt-pct				MgO, by difference, wt-pct	Bulk density, g/cm^3
	SiO_2	Al_2O_3	Fe_2O_3	CaO		
England:						
South Yorkshire.......	2.50	1.21	1.64	57.60	37.05	3.00
South Durham..........	2.35	1.42	1.40	58.20	36.12	2.85
South Wales...........	2.58	1.30	1.67	56.06	38.39	3.00
North Derbyshire......	.88	.45	1.30	56.80	40.57	3.10
Pelletized doloma.....	.83	.44	1.14	56.70	40.89	3.25
West Germany............	1.00	.30	1.50	NAp	[1]36.0	3.15
Italy...................	1.05	.92	.28	56.10	41.50	3.20
France..................	.70	.45	.60	57.20	41.05	3.10
Japan...................	.60	.60	3.00	62.50	33.30	3.00
United States (low flux)	.40	.30	.30	56.90	40.40	3.25
United States (standard)	1.10	.60	1.20	51.80	38.0	3.20

NAp Not applicable. [1]Minimum.

humidity of 85 pct. After 24 hr, the material was removed, dried, and screened at 35 mesh to determine the amount of material passing through. The rate of hydration was found to be dependent on the heat treatment the dolomite had received, on the amount of iron oxide in the dolomite, on the dolomite grain sizing, and on the number of broken grains present.

BRICK PROCESSING

The majority of dolomite brick is used in the form of either pitch-bonded or tempered, although others are of the burned-impregnated type. A limited number of fired dolomite brick containing no carbon are used in rotary cement kiln linings and electric furnace linings, although direct-bonded magnesia-chrome bricks have generally been the accepted refractory products for both these applications. Kappmeyer (11) presented a survey of the carbon-containing types of bricks. The processing of the unburned types consists of preheating the sized refractory grain and the pitch material separately, mixing these two materials in a heated mixer, and pressing brick shapes at 4,000 to 10,000 psi on mechanical presses.

The amount of pitch varies and is an important influence on the properties of the brick. Generally, to obtain the desired combination of maximum brick density and maximum residual carbon, the amount of pitch will be 5.0 to 6.75 wt-pct. The type of pitch has an important influence on the strength of the brick at the low temperatures associated with part of the burn-in cycle. Brick with excessive pitch has low strength for a short time at low temperatures and has collapsed under its own weight.

After the brick is pressed, it is cooled for storage or taken directly to ovens for tempering. Tempering of the pitch-bonded brick improves several characteristics. The low-temperature hot strength of the brick is markedly increased, eliminating concern about possible failure of the lining during burn-in. Also, tempering results in a significant improvement in the resistance of the brick to hydration. By tempering, the safe storage period for dolomite brick can be extended from only a few days to several weeks. The temperatures involved in tempering generally range from about 90° to 650° C, but are more commonly 230° to 315° C. Exposure times range from 30 min to 48 hr, with the shorter time being associated with the higher temperatures.

Pitch-impregnated brick is produced by forcing pitch into the open pores of a presintered (burned) brick made from dolomite grain aggregates. The properties of the burned brick may vary widely according to composition and degree of heat treatment before impregnation. The burned brick may be impregnated with pitch to some extent simply by dipping the brick into liquid pitch at 120° to 315° C, but more commonly it is impregnated by using a vacuum pressure system to accelerate the rate at which the pitch is forced into the brick pores.

The quantity of pitch picked up by a brick is directly related to the initial porosity of the brick. The residual carbon content in the brick naturally increases with greater pitch content and/or increased pitch softening point. However, because brick porosity is confined to a narrow range to achieve other desirable properties, the quantity of pitch that can be introduced is limited. With this limitation, it is desirable to use pitch with the highest softening point compatible with the operating characteristics of the vacuum impregnating system.

It is interesting to compare the amount of energy required to produce tempered brick with that required for impregnated brick. Production of impregnated brick requires 1.64 million Btu/ft^3 which is 20 to 30 pct more energy than for the same volume of tempered brick (1.35 million Btu). Also, experience indicates that properly made tempered brick can give service life equivalent to that of the impregnated, burned brick.

BRICK USAGE

United Kingdom

Leonard (15) reviewed BOF lining practices in the United Kingdom. Both dolomite and magnesite were used. There has been a trend towards magnesia enrichment of dolomite refractories by additions of magnesite. Improvements in the quality of dead-burned dolomite and bricks made from it were achieved by more selective quarrying and blending of deposits and the greater use of rotary kilns and shaft kilns with higher firing temperatures. It became possible to produce grain of such consistent chemistry and density that silica content was restricted to 1 pct and densities of over 3.0 g/cm^3 were achievable.

Spencer (24) reported that in 1970, pelletized dead-burned dolomite grain was introduced in England. This arose because most of the highest purity dolomite in the United Kingdom is difficult to sinter to high densities in a single firing process. The decomposition of high-purity dolomite to an active oxide followed by pelletizing under high pressures and sintering results in densities in the 3.25- to 3.30-g/cm^3 range. Of course, this two-stage firing process has the disadvantage of increased costs. With the introduction of this pelletized dead-burned dolomite, linings gave improved furnace performances of approximately 10 to 15 pct.

Europe

Hardy (6-7) discussed BOF linings and lining wear from the standpoint of a steelmaking consumer. In Europe, a long history of basic Bessemer steelmaking resulted in the establishment of raw dolomite as standard lining materials. The first major change in usage patterns came with the advent of big capacity furnaces. The danger of slumping during burn-in is greater with big vessels and, therefore, almost all vessels in Europe of 200-ton capacity or more used tempered blocks. Magnesia-enriched tempered dolomite and, in some cases, tempered magnesite have been used in selected zones to combat slag attack.

Japan

Hardy (6) and Leonard (15) both described the improvements in Japanese steel refractories. In Japan, which lacks suitable reserves of most raw materials, the practice has been to use synthetic magnesia-dolomite clinkers and seawater periclase in BOF refractories. From the late 1950's until about 1970, the average MgO content of BOF linings increased from 50 to 60 pct up to 80 to

90 pct. This is indictive of increased usage of high magnesia coclinkers and of seawater periclase. In 1976, refractory consumption in BOF vessels of enriched dolomite was about one-half that of periclase. Dolomite bricks were initially pitch-bonded, but fired mixtures with periclase were introduced in the late 1960's. By the early 1970's, the use of MgO-enriched dolomite was well advanced, first as pitch-bonded, then as fired brick. In Japan, both slag testing and thermal shock resistance testing have been used for evaluating refractories for BOF linings. Both authors stress the extremely long lining lives, over 1,000 heats, being achieved in Japanese steel plants resulting, in part, from strict control of slag chemistry and gunning maintenance.

United States

It is logical to discuss dolomite brick usage in terms of iron and steelmaking since this usage constitutes between 50 and 70 pct of the total output of the refractories industry. Kappmeyer (12) estimated that of refractories used in the steel industry, about 3 pct are consumed in coke ovens, 10 pct in blast furnaces, 60 pct in BOF's, 12 pct in pouring pits, and 15 pct in continuous casting, rolling, and other forming operations. World steel production, broken down by process, is shown in table 5. It is interesting to observe the change in types of refractories used in the BOF steelmaking process. Table 6 presents the approximate distribution of BOF brick used in the United States.

TABLE 5. - Distribution of steel production by process, million tons (12)

Process	1960	1971	1985
Bessemer	47	21	10
Open hearth	261	230	90
BOF/O-BOF	13	272	850
Electric	39	94	240
Total[1]	379	627	1,200

[1]Some other processes are included in the total.

TABLE 6. - Approximate distribution of BOF brick usage in the United States, percent (12)

Brick	1967	1970	1980
Tempered periclase	10	30	40
Burned impregnated periclase	32	29	20
Magnesite, all types	41	24	25
Dolomite, all types	17	17	15

Kappmeyer (11) compared the properties of dolomite-containing steel plant refractories of both the tempered and burned-impregnated types. These property comparisons are shown in table 7. While the burned brick has lower levels of residual carbon, this type shows higher resistance to slag erosion. Although few dolomite-containing brick are used in the burned condition, substantial amounts are used as pitch-bonded or tempered.

In 1980, Marr (16) surveyed the applications of dolomite materials as refractories. Marr stated that dead-burned dolomite is used in the form of both monolithic products and brick products. Dolomite gunning mixes have been used extensively, especially in electric arc furnaces. Hearths of both open hearth and electric furnaces have been made of rammed dolomite. Tar-bonded dolomite bricks have been found to be satisfactory for BOF linings particularly when used in combination with magnesite bricks. The combining of continuous casting and ladle refining processes in steelmaking is common now and results in higher ladle operating temperatures and basic slags. Therefore, traditional clay and alumina bricks are being replaced by basic products, quite often, dolomite.

Other applications in which fired dolomite brick has performed well are argon-oxygen-decarburization (AOD) furnaces, cement and lime rotary kilns, and nickel or copper refining smelters.

The swing to low-cost dolomite brick in the United States never reached the level predicted around 1965. Peatfield and Spencer (18), in 1979, in discussing

TABLE 7. - Dolomite brick properties

Brick type and sample	Chemical composition, wt-pct					Bulk density, g/cm³	Hot modulus of rupture, psi		Residual carbon content, wt-pct, after coking to--		Slag erosion[1]
	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2		1,200° C	1,980° C	1,090° C	1,650° C	
Tempered dolomite:											
TD-1....	40.4	56.9	0.3	0.3	0.4	2.84	NAp	NAp	3.8	2.6	2.4
TD-2....	40.0	55.9	.0	.2	.8	2.84	NAp	NAp	3.4	2.7	2.5
TD-3....	40.2	55.6	.9	.2	.6	2.84	NAp	NAp	3.4	2.7	3.2
TD-4....	40.8	56.5	.2	.1	.3	2.84	NAp	Nap	3.7	2.5	3.6
Tempered dolomite periclase:											
DPT-1...	60.2	37.9	.3	.3	.6	2.96	NAp	NAp	Nap	2.8	Nap
DPT-2...	57.5	37.4	3.3	.5	2.0	3.01	NAp	NAp	NAp	2.6	NAp
DPT-3...	61.2	36.1	.6	.3	1.4	2.95	NAp	NAp	NAp	3.0	NAp
Burned impregnated dolomite:											
ID-1....	40.8	57.9	.2	.2	.6	3.14	1,865	610	NAp	1.5	1.3
ID-2....	42.0	55.5	.3	.5	.6	3.06	1,080	550	NAp	.9	1.2
ID-3....	40.2	55.6	.8	.2	.6	3.04	1,860	380	NAp	.8	1.1
Burned impregnated dolomite periclase:											
IDP-1...	66.9	31.6	.1	.2	1.2	2.98	910	680	NAp	1.3	1.1
IDP-2...	60.0	38.3	.2	.2	.7	3.12	865	370	NAp	1.5	.8

Nap Not applicable.
[1]Relative depth of brick eroded away as compared with established standards.

basic raw materials for steelmaking refractories, mentioned that dolomite- and magnesia-based materials are the only materials that are readily available and cost effective. The selection between magnesia- and dolomite-based products depends not only on the technical merits of the materials and lining life requirements, but also on their relative economies. For example, magnesia products in the United States are only 40 to 50 pct more expensive than dolomite products, whereas in Europe, they are 200 to 300 pct more expensive. This reason has been quoted for the greater development of dolomite in England. The absence in the United States of a strong basic Bessemer tradition is probably another important reason.

PROPERTIES OF 14 U.S. DOLOMITES

MATERIALS AND TEST PROCEDURES

Samples of 14 different raw dolomite samples were obtained from sources in Alabama, Ohio, Pennsylvania, Missouri, Michigan, California, and Wisconsin. Eight of these materials were obtained from suppliers of refractory grade dolomites, while the other six were representative of dolomites that are used for nonrefractory applications. Approximately 50 lb of each sample was received. Representative portions of each sample were used in the various characterization studies. Powdered samples were sent to an independent analytical laboratory for chemical analysis and loss on ignition (LOI) determinations according to the procedures of ASTM 0574-71. Mineralogical analyses were conducted on minus 325-mesh material by X-ray diffraction. Differential thermal analysis (DTA) and thermogravimetric (TGA) curves were obtained on the materials using a commercially available thermal analyzer. Apparent specific gravities were measured using an air comparison pycnometer. Petrographic analyses and cathodeluminescent photographs were made on thin sections from each material.

RESULTS AND DISCUSSION

The results of the chemical analyses and loss on ignition, apparent specific gravity, and mineralogical determinations are shown in table 8; petrographic analysis data are given in table 9. All 14 of these samples meet the chemical requirements for refractory grade dolomites as specified in table 2. Only three of the samples had impurity contents totaling over 2.0 wt-pct with the major impurities being either SiO_2 or Fe_2O_3. The theoretical LOI value for pure dolomite is 47.72 wt-pct. All of the samples had LOI values over 45.0 wt-pct, and seven had LOI values greater than 47.0 wt-pct. The most predominant accessory minerals were quartz and calcite. The apparent specific gravity values were all between 2.81 and 2.87. This property measurement, when greater than 2.80, is usually a good indication of dolomite that can be fired to high-grain density.

Photomicrographs of four of the samples are shown in figures 1 through 4. These photomicrographs illustrate the wide range in grain sizes and microstructures of the various dolomites.

The microstructure of sample Ohio No. 1 (fig. 1) is characterized by small grains (average diameter of approximately 100 µm) having no twinning and with poorly

TABLE 8. - Properties of raw domestic dolomites

Source and sample	Chemical analysis, wt-pct						Apparent specific gravity, g/cm^3	Accessory mineral phases[1]	Hydration,[2] wt-pct	Calculated liquid phase, wt-pct
	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	Loss on ignition				
Alabama:										
1.......	20.80	30.19	1.12	0.56	0.22	46.68	2.87	Q,C	83.5	10.4
2.......	20.39	30.13	1.11	.39	.31	47.30	2.86	Q	80.9	9.8
3.......	20.12	30.52	1.48	.82	.27	46.47	2.85	Q,C	48.4	15.2
Ohio:										
1R......	21.20	30.61	.02	.11	.06	47.54	2.87	Q	100.0	.5
2R......	19.46	29.57	1.69	.83	2.99	45.05	2.84	Q	ND	
3R......	20.99	30.13	.40	.68	.12	47.26	2.87	Q	100.0	8.9
Pennsylvania:										
1R......	21.26	27.61	.16	.06	.30	46.41	2.85	Q	72.6	2.3
2R......	21.01	30.76	.29	.22	.39	47.08	2.86	Q,C	95.1	4.2
3.......	21.22	30.83	.15	.20	.22	47.06	2.81	C	58.3	2.3
Michigan:										
1.......	21.18	30.61	.49	.08	.10	47.19	2.84	Q,C	98.6	4.6
2.......	20.95	30.34	.52	.08	.19	47.42	2.84	Q,C	ND	ND
Missouri:										
1R......	19.20	31.16	.31	.12	3.61	45.44	2.84	Q,C	5.4	13.8
Wisconsin:										
1.......	21.16	30.78	.27	.04	.18	46.95	2.86	Q,C	99.5	2.3
California: 1..	21.70	31.07	.50	.07	.15	45.85	2.82	Q,C	98.8	4.2

R Refractory-grade dolomite. ND Not determined.

[1] Q, quartz; C, calcite. [2] As determined per ASTM C492-66 (1981).

TABLE 9. - Petrographic analysis data for raw domestic dolomites

Source and sample	Crystallinity[1]	Grain size, mm	Formation and age	General description
Alabama:				
1..........	I	0.06 -0.18	Ketona, Upper Cambrian.	Patchy areas of coarse crystals, not equigranular, some dark organic material.
2..........	I	.25 -1.25		Equigranular, curved grain boundaries, no trace of original texture.
3..........	I	.18 -1.25		Coarse crystals along fractures, not equigranular, no trace of original texture.
Ohio:				
1R.........	I	.04 - .18	Guelph, Silurian.	Not equigranular, patchy zones of coarse crystals, porous.
2R.........	I	.125- .375		Not equigranular, contacts wavy, slightly dirty, organic material along stylolites, voidy.
3R.........	I	.06 - .375		Equigranular, dirty, wavy contacts, porous, pores may contain organic material.
Pennsylvania:				
1R.........	P	.06 - .375	Ledger, Lower Cambrian.	Not equigranular, irregular grain boundaries, wavy grain boundaries with cloudy centers.
2R.........	P	.125-1.0		Some circular patches of fine grains, some pressure-induced twinning; no indication of original texture.
3..........	P	.125-1.0		
Michigan:				
1..........	P	.06 - .18	Engadine, Middle Silurian.	Equigranular, wavy contacts, porous, dirty.
2..........	P	.125- .75		Do.
Missouri: 1R	I	.06 - .375	Bonne Terre, Upper Cambrian.	Not equigranular, excellent zoning, could be areas of iron, very cloudy, an altered subtidal limestone, perhaps oölitic circular patterns.
Wisconsin: 1	I	.04 - .675	Niagara, Middle Silurian.	Finely crystalline, poorly sorted crystals, not equigranular, no trace of original structure.
California:				
1..........	P	1 -5	Sur, Jurassic.	Coarsely crystalline, twinned, equigranular contacts straight, clear crystals.

R Refractory-grade dolomite. [1]I, intermediate; P, poor.

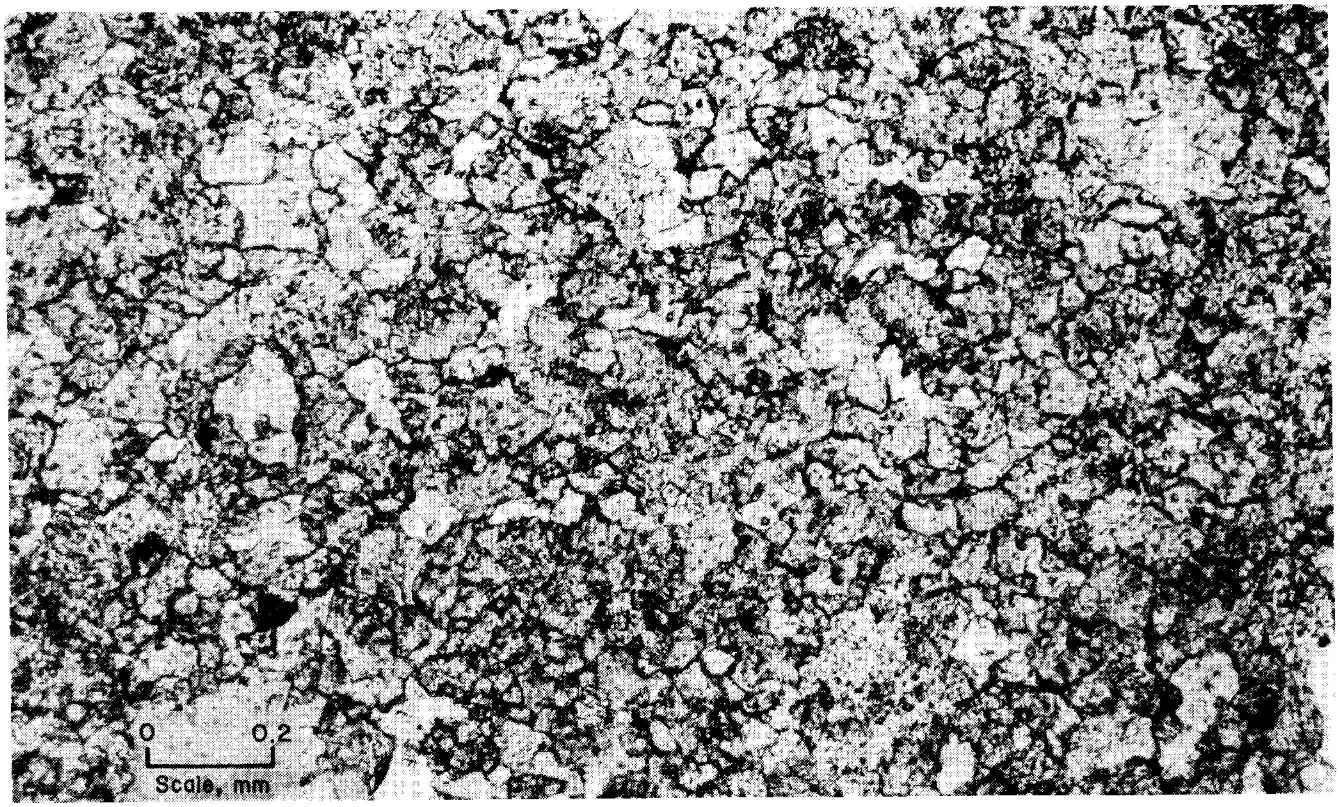

FIGURE 1. - Photomicrograph of Ohio dolomite No. 1 presently used to produce refractory products.

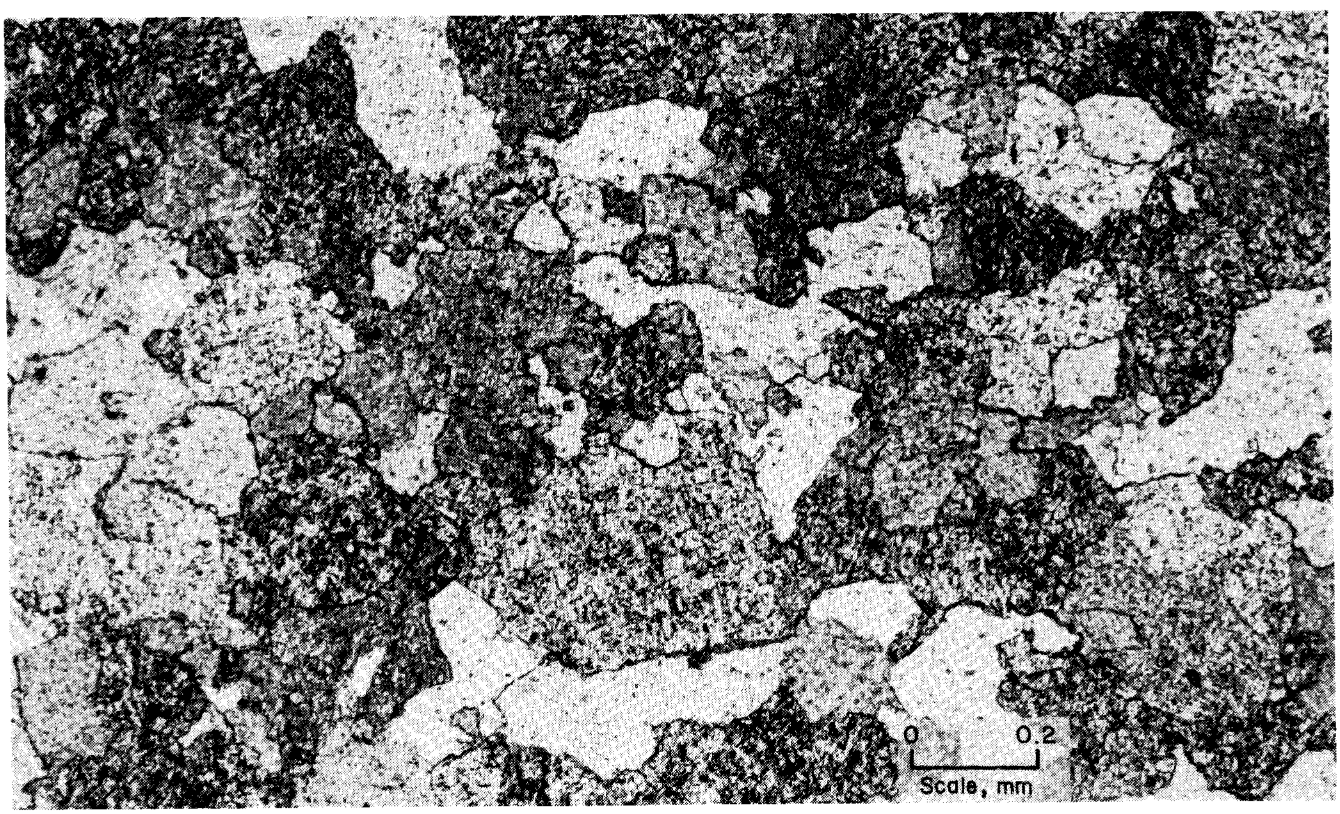

FIGURE 2. - Photomicrograph of Missouri dolomite presently used to produce refractory products.

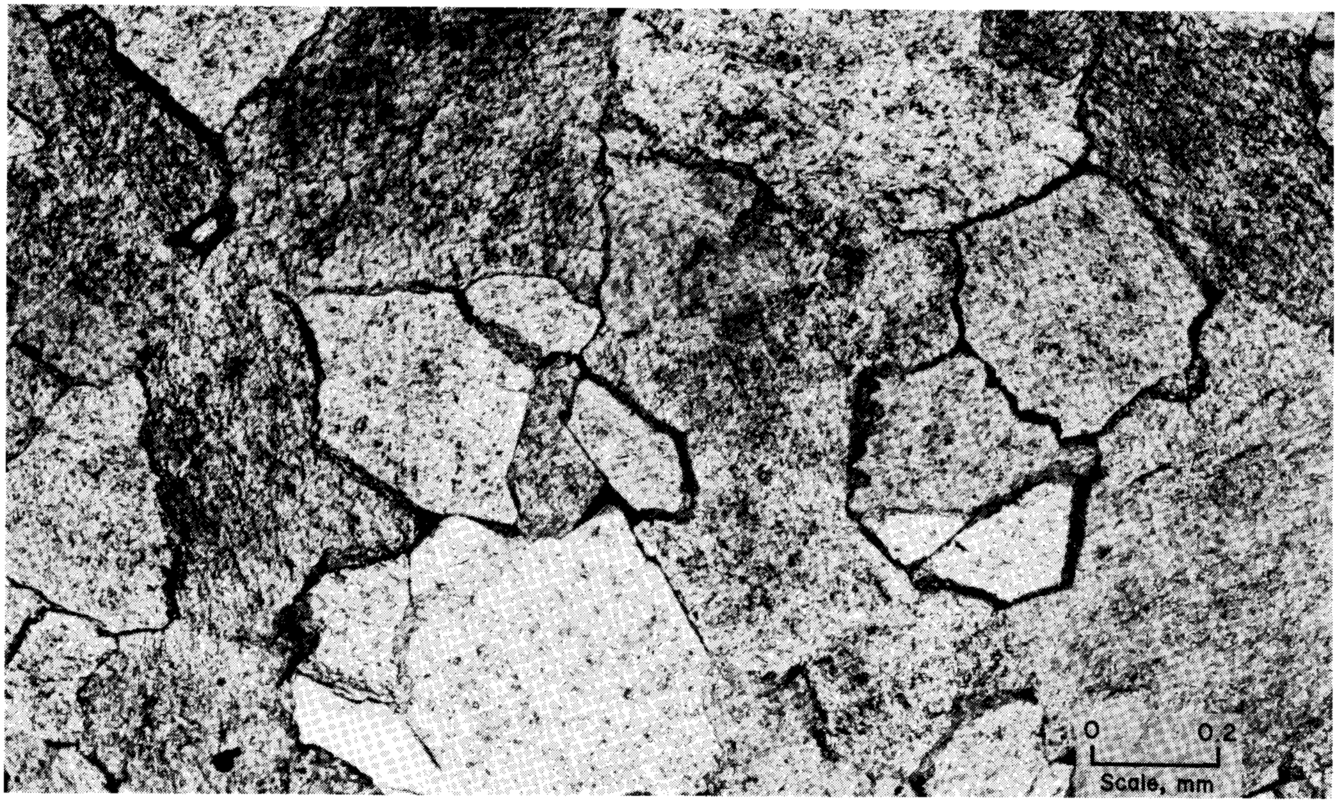

FIGURE 3. - Photomicrograph of Alabama dolomite No. 3.

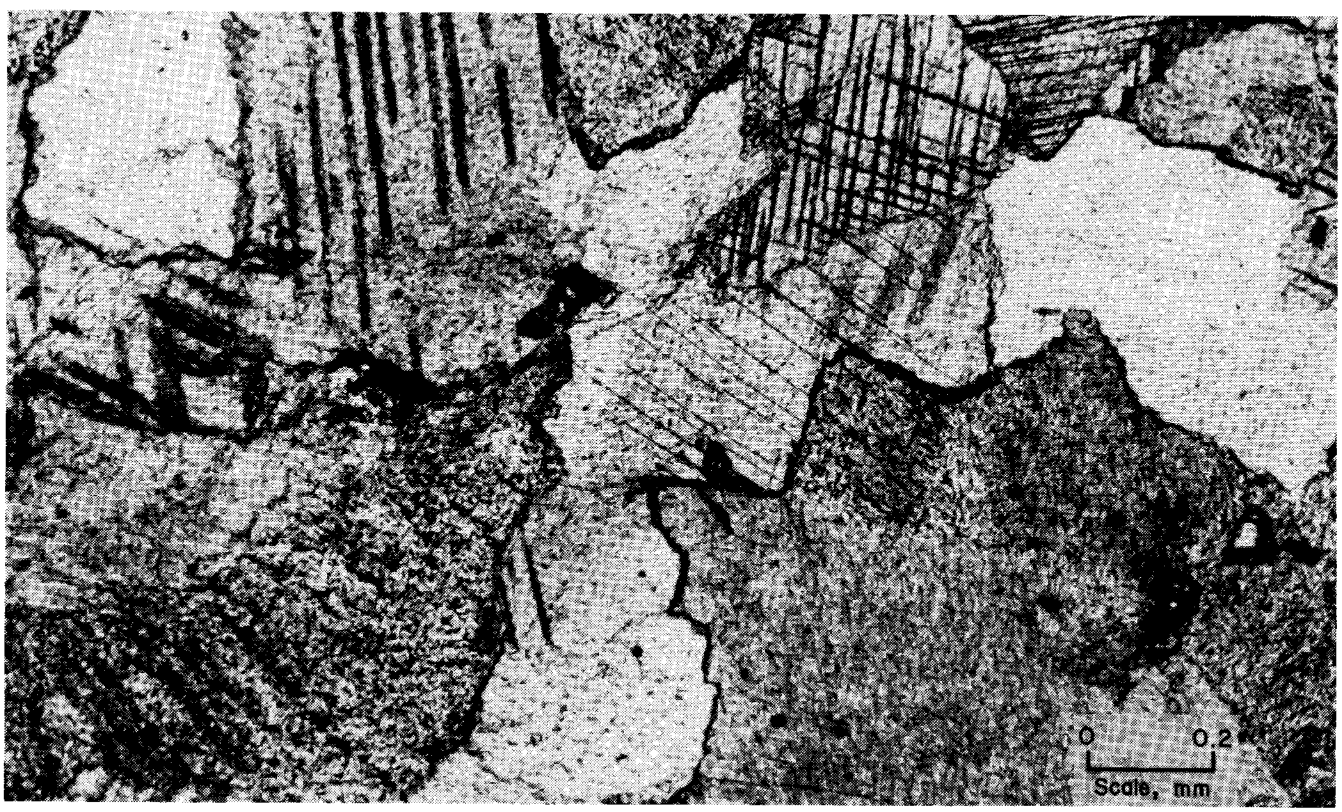

FIGURE 4. - Photomicrograph of Pennsylvania dolomite No. 3.

defined grain boundaries. The microstructure of sample Missouri No. 1 (fig. 2) consists of medium-sized grains (average diameter of approximately 300 µm) having no twinning and with better defined grain boundaries. The microstructure of sample Alabama No. 3 (fig. 3) consists of large, angular grains (average diameter of approximately 600 µm) having no twinning and with well-defined boundaries. The microstructure of sample Pennsylvania No. 3 (fig. 4) consists of large, angular grains (average diameter of approximately 750 µm) having a large number of twinned grains or striations and with well-defined grain boundaries.

Of the 14 raw dolomites characterized in this investigation, only two (Pennsylvania No. 2 and 3) are suitable for calcining to high-density, dead-burned grain in a single-step firing process. While these two samples did not exhibit any marked differences from the other dolomite samples with regard to chemistry, mineralogy, or thermal decomposition, they contain the largest grain sizes of all the materials observed. Besides having grains that are approximately twice the size of those of most of the other samples, these two samples also contain a large number of twinned grains, as can be seen in figure 4. While it cannot be assumed that either the larger grain size or the twinned grains have any influence upon the calcination and densification characteristics of these two dolomite samples, further investigations into the fired grain processing and properties may provide the answers.

Examples of the thermal analysis data are shown in figures 5 through 7. With regard to DTA data, it is possible to group the dolomites by the similarities in the endothermic peak locations, as has been done with the curves in figure 6. Thus, it is evident in figure 6 that three of the Alabama materials behave similarly upon heating. Comparing the DTA curves in figure 5, it is seen that the two Michigan dolomites have large peaks around 880° C as do most of the other dolomites, but both of the Michigan materials have a small peak around 650° C, which none of the other materials exhibit. All the DTA curves for these materials indicate typical endothermic peaks exhibited by most dolomite materials. The sharper, lower temperature peak ranging from 780° to 820° C corresponds to the decomposition of $MgCO_3$, and the broader, higher temperature peak ranging from 860° to 920° C corresponds to the decomposition of $CaCO_3$.

Examples of typical TGA curves are shown in figures 8 and 9. While the DTA curves have separate peaks representing a two-step decomposition process, the TGA curves, which were run at half the heating rate of the DTA scans, indicate only a single step decomposition. The total weight losses for these dolomites coincide well with the LOI values reported in table 8. The TGA weight loss for Michigan dolomite No. 1 was 47.62 wt-pct versus 47.19 wt-pct LOI, and the TGA weight loss for Pennsylvania dolomite No. 2 was 47.78 wt-pct versus 47.08 wt-pct LOI.

It is anticipated that when the refractory properties of the calcined grain produced from the 14 different dolomites are determined that these properties can be related to differences in the chemical compositions, and especially the differences in microstructure and thermal decomposition of the raw dolomites.

SUMMARY

A review of the literature on dolomite resources showed that large quantities of high-purity dolomite materials exist in the United States. Most of these deposits are located in the area around the Great Lakes as well as in Pennsylvania, Alabama, California, and West Virginia. Many of these resources have been used to provide dolomites suitable for various uses other than refractory products. A few of the deposits have proven useful as refractory grade dolomites. Besides meeting requirements for high purity levels, refractory grade dolomites also must

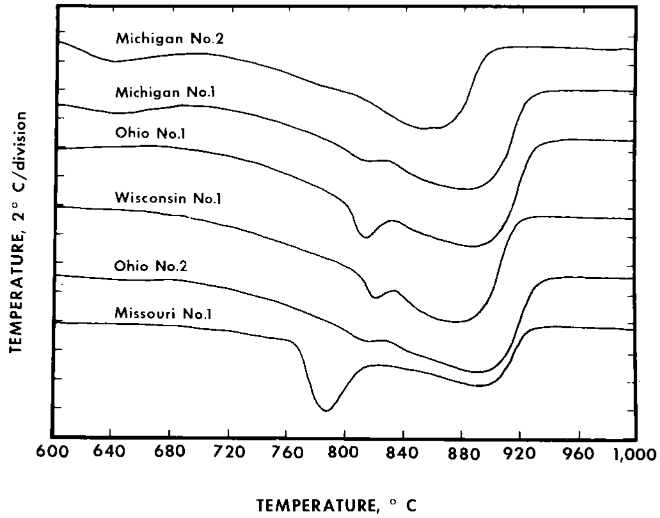

FIGURE 5. - DTA curves for six dolomites.

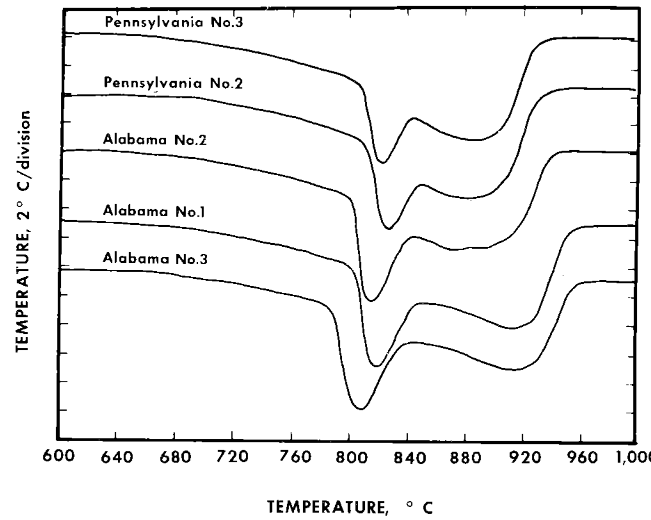

FIGURE 6. - DTA curves for five dolomites.

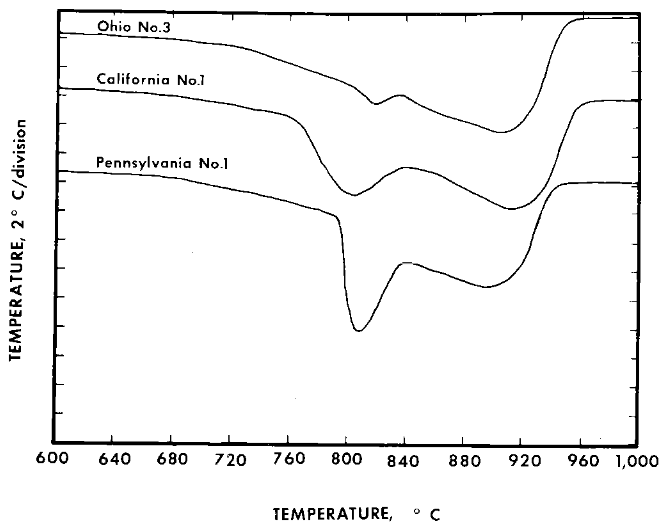

FIGURE 7. - DTA curves for three dolomites.

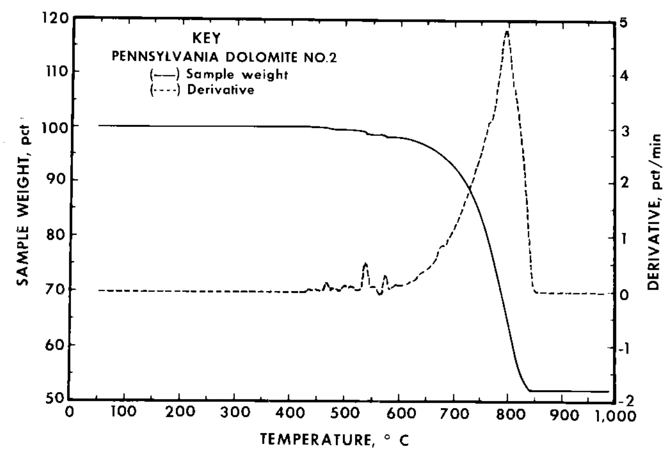

FIGURE 8. - TGA curve for a sample of Pennsylvania dolomite No. 2.

meet requirements for high grain density and resistance to hydration.

The ideal refractory grade dolomite material is one that can be calcined in a single pass through a kiln. Since very few such sources are available, some dolomite producers have introduced a two-step firing process consisting of a low-temperature calcination followed by briquetting and a high-temperature firing. The double-firing process adds significantly to the price of the resultant grain.

Another product that dolomite producers have developed is an MgO-enriched dolomite coclinker. By adding periclase powder to the dolomite before the briquetting operation, a grain of higher MgO content and thus improved slag resistance can be produced.

The European countries, especially England, have led in the increased usage of dolomite refractories. This fact has been attributed to the greater price differential between dolomite and periclase in Europe versus the United States and to a traditionally greater use of Bessemer converters for steelmaking in Europe.

An investigation of 14 raw domestic dolomites was conducted with the purpose of characterizing these materials and comparing their properties with the

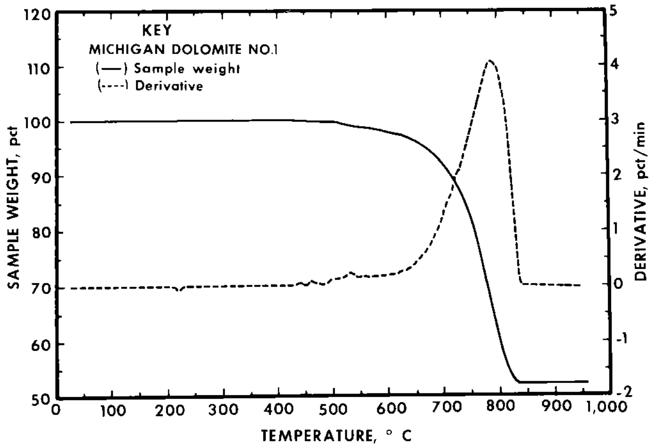

FIGURE 9. TGA curve for a sample of Michigan dolomite No. 1.

refractory properties of calcined grain produced from them. The raw materials were characterized as to chemical, physical, and thermal properties. All of the materials contained at least 49.0 wt-pct combined MgO and CaO. Raw apparent specific gravities ranged from 2.81 to 2.87 and the raw bulk densities ranged from 2.55 to 2.80 g/cm^3. The major accessory minerals associated with these dolomites were calcite and quartz.

The thermal analyses of the materials were characterized by two endothermic peaks, one occurring between 780° and 820° C and the other occurring between 860° and 920° C. Examination of thin section photomicrographs of the raw dolomites indicated that the average crystallite grain size ranged from around 100 µm up to about 750 µm. The microstructures of two Pennsylvania dolomites that are suitable for calcining to high density dead-burned grain in a single firing were characterized by the largest average crystallite grain sizes and by a large number of twinned grains. It is possible that the large grain sizes and occurrence of twinned grains has some influence upon the calcination and densification of these dolomites. Further investigations into fired grain processing and properties may resolve this question.

With the large reserves of high purity dolomite in the United States and the price advantage that dolomite holds over seawater periclase, it appears that the U.S. refractory practice should move toward higher dolomite usage.

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