Development of Lightweight Insulating Refractories for Steelmaking and Other High-Temperature Process Industries

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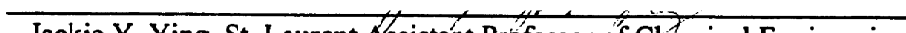
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ABSTRACT

New castable refractories are developed for steelmaking and other high-temperature process industries using a new raw material from Alcoa Industrial Chemicals. This new material, marketed under the tradename Plasmal™, is a novel synthetic ceramic oxide, consisting primarily of anhydrous α-alumina (α-Al_2O_3) with magnesium aluminate spinel inclusions ($MgO \cdot Al_2O_3$). Its microstructure is highly porous which imparts low thermal conductivity and grain densities of 1.8 to 2.0 g/cm^3 (112 to 125 lbs/ft^3). Grain porosities range from 45 to 50 percent.

Castable refractories developed in this thesis incorporate high-purity calcium aluminate cements and expanded minerals with the Plasmal™ aggregate. Some formulations include kaolin clay to increase the plasticity of the uncured castable. These refractories possess dried bulk densities under 1.7 g/cm^3 (105 lbs/ft^3) and exhibit minimal shrinkage (less than 1.5 percent) at temperatures up to 1650 °C (3000 °F). Density and temperature stability of the refractory can be systematically changed by adjusting the proportions of these components.

The market for refractories with these particular thermal stability and density properties appear promising, especially as steelmaking and other process technologies continue to raise processing temperatures to increase operating efficiencies. Furthermore, only 10 percent of all insulating castables on the market today can be used at 3000 ° F or higher, most of which require expensive raw materials such as bubble alumina. Thus, the refractories developed here offer a basis for creating new products to meet this need.

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Abbreviations

ACI	American Concrete Institute
ASTM	American Society for Testing and Materials
Btu	British thermal unit
°C	degrees Celcius
CA	calcium aluminate
cm	centimeter
CTE	coefficient of thermal expansion
°F	degrees Fahrenheit
ft	foot
g	gram
hr	hour
in	inch
k	thermal conductivity
LAC	lightweight aggregate concentration
lbs	pounds
m	meter
min	minute
ml	milliliter
MOR	modulus of rupture
pcf	pounds per cubic inch
psi	pounds per square inch
q	heat flux
std. dev.	standard deviation
T	temperature
wt %	weight percent
μ or μm	micron

1.0 Introduction

Advanced societies and economies depend on manufacturing processes conducted at high temperatures. Economic production of basic materials such as steel, aluminum, glass, cement, and many organic chemicals require processing steps at temperatures over 1,000 °F. Virtually everything we eat, drink, wear, occupy, or enjoy rely on high-temperature processes somewhere in their production or distribution. The manufacture of steel, for example, requires several high-temperature operations including melting and refining virgin or scrap feedstocks in basic oxygen or electric arc furnaces.[1] The resultant steel is used in the automobiles that provide our transportation, in the processing equipment that produce our food, and in the buildings that house our work and education.

Refractories make high-temperature manufacturing possible and economical, and thus have been called "enablers" or "facilitators" of our economic productivity.[2] Process engineers rely on these heat-resistant materials to confine heat energy, hot gases, molten metals, and molten ceramics. Refractories are shaped into furnace liners, insulation for high-temperature catalytic reactors, crucibles, kiln furniture, and other high-temperature articles. In short, refractories are deployed wherever heat and high temperatures must be managed or isolated.

Refractories can be defined as materials which retain their physical shape, structural integrity, and chemical identities in the presence of thermal, mechanical, and chemical stresses for some period of time, ranging from minutes to years.[3,4] In process applications, these stresses often include high temperatures, corrosive gases and melts,

thermal shock, physical impact and abrasion, mechanical loads, and erosion from fluid turbulence of molten metals and ceramics. The service life of refractories is finite and varies depending on the severity of their environments. In this sense, refractories are sacrificial materials which must be periodically replaced.

Chemically, refractories are a class of technical ceramics, consisting of complex combinations of high-melting crystalline oxides. Carbides, carbon, graphite, and other nonoxides may also be incorporated into a refractory product depending on its service needs. Being polycrystalline ceramics, refractories are characteristically brittle with high elastic moduli, and are generally stronger in compression than in tension.[5] Their strength can vary considerably owing to local variations in refractory microstructure and lack of ductility.[6]

Refractories are produced from both natural minerals and synthetic (i.e., processed) materials. Among commonly-used natural minerals are silica, bauxite, fireclay, kaolin, kyanite, chromite, olivine, dolomite, and magnesite. The use of mineral derivatives and synthetic feedstocks have increased over the past several decades as improvements in steelmaking and other process technologies have demanded higher and more consistent refractory performance.[7] These feedstocks include alumina, magnesia, silicon carbide, mullite, graphite, and zirconia. Refractory raw materials pertinent to this thesis are discussed in Sections 2.4 and 6.3.

Refractory metals such as titanium, tantalum, and tungsten are capable of withstanding temperatures well over 1,000 °F, and thus serve important engineering applications.[8,9] However, in materials processing environments, metals often readily

corrode in the presence of molten solids, and would be much more expensive to use than nonmetallics, technical limitations notwithstanding. Consequently, industrial refractories are almost invariably ceramics. The discussion in this thesis will therefore focus exclusively on nonmetallic refractories as used in high-temperature manufacturing processes such as steelmaking.

Total worldwide sales of process refractories by domestic and international producers in 1994 exceeded $5.2 billion.[10] Countries with a substantial refractory manufacturing industry include the United States, United Kingdom, Germany, France, Russia, and Japan. In the United States, over 100 firms produce refractories. Company size ranges from less than 10 individuals to large publicly-held corporations with over 1,000 employees and substantial research, engineering, and manufacturing facilities. Among the largest U.S. producers are Indresco, Baker Refractories, Premier Refractories and Chemicals, A. P. Green Industries, National Refractories and Minerals, Adience, and Resco Products (see Figure 1-1). In 1994, the U.S. Department of Commerce reported that domestic firms manufactured over 10 billion pounds of refractory products with a value of approximately $2 billion.[11]

The largest international manufacturing firms are the Didier-Werke AG (Germany), Compagnie de Saint-Gobain (France), Shinagawa Refractories (Japan), Hepworth Refractories Ltd. (United Kingdom), and TYK (Japan) (see Figure 1-1). Some international companies produce refractories in the United States such as Didier-Werke which, through its ownership of North American Refractories Company, operates ten plants in the U.S.[12] Imports of refractories into the U.S. market are relatively small. In

$739.0 million* **Didier Group**
Wiesbaden, Germany (publicly held)
Dietrich von Knoop, chair/ CEO
Zircoa Inc., NARCO
"The worldwide steel economy continues its marked upswing." The positive effect on the refractories industry has helped to lower the over capacity burden. North American Refractories sold the Canadian branch to NARCO Canada and the continuous casting business was merged with Interstop Corp. to form InterTec.

$480.0 million* **Veitsch Radex-AG**
Vienna, Austria (publicly held)
Dr. Günther Mörtl, CEO
Veitsch-Radex Urmitz GmbH
Parent company is Radex-Heraklith Industriebeteiligungs AG. This giant constructed a new brick plant for rotary cement kiln refractories. Business outlook: "Good economic situation of the target industries. Excellent sales, price situation not satisfying."

$465.0 million* **Shinagawa Refractories Co. Ltd.**
Tokyo, Japan(privately held)
Masami Takeda, president
Shinagawa Rozai Co., Tiokoku Yogyo Co. Ltd.
The company sold two factories and used the proceeds to modernize their five remaining factories including a new plant for basic brick which "is beyond the concept of conventional ones."

$463.0 million* **Compagnie de Saint-Gobain**
Paris, France(publicly held)
Jean-Louis Beffa, chair/CEO
Corhart, Refradige, Nuova Sirma, Norton , Sovoie Refractories, SEPR
This giant tripled profits in 1994 due to increased sales, restructuring, and increased productivity. Sales are improving in 1995.

$400.3 million **The Morgan Crucible Co. Ltd.**
Windsor, England (publicly held)
Dr. E. B. Farmer, CEO
The Thermal Products Group benefited from strong growth on new products, improved economic conditions in the United States and improving demand in Europe.

$261.3 million **Asahi Glass Co. Ltd.**
Tokyo, Japan (publicly held)
Hiromichi Seya, president
"Our performance was hindered by further output declines at many steel, nonferrous metal, glass and cement companies." Sales increased in Southeast Asia. Some fine ceramics are included in refractory sales figure.

$250.0 million **The Carborundum Co.**
Niagara Falls, NY (publicly held)
Luiz F. Kahl, president
Business outlook: "growing 5-10% in '95. Excellent year for capital purchases. Steady but much slower growth" in 1996.

$250.0 million **Vesuvius Group**
Brussels, Belgium (privately held)
Gian Carlo Cozzani, CEO
Vesuvius-McDanel, Vesuvius-Zyalons, Leco Corp.-Tech. Cer. Div., Kawasaki-Vesuvius Adv. Refractory Technology JV
Vesuvius is part of Cookson Group Plc. The company built plants for continuous casting refractories in Trinec, Czechoslovakia; Ako, Japan; and Calcutta India. Business outlook: "generally good due to continued health of steel industry in North America.

$243.0 million **Indresco Inc.**
Dallas, TX. (publicly held)
J. L. Jackson, CEO
Harbison-Walker Refractories
Sales include the company's mineral division. In April 1994, the company purchased REFMEX, the largest refractories manufacturer in Mexico. Chile's largest manufacturer, RECSA, was acquired early this year. New facilities were provided for MgO-carbon and high alumina brick and low cement castable manufacturing.

$213.0 million **Hepworth Refractories plc**
Sheffield, England (publicly held)
C. John Carter, CEO
Hepworth Refractories Ltd., Hepworth Refractories (Belgium) S.A., Les Produits Siliceux S.A., Constructions Thermique Europeennes S.A.
Hepworth continued to suffer from over-capacity in the international refractories market. However, sales development improved sales into 1995. Duraflow free-flow low cement castables were introduced in 1994.

$189.0 million **TYK Corp.**
Tokyo, Japan (privately held)
Susumu Ushigome, CEO
TYK Refractories
Sales were hurt by the strong yen and inexpensive imports. These same factors will continue to hurt sales into 1996.

$178.0 million **Baker Refractories**
York, Pa. (privately held)
David F. Manchester, president
Sales continue to increase for this giant—"should be a good year." A new magnesia-3 zirconia brick for the transition zone of rotary cement kilns was introduced.

$160.9 million **A. P. Green Industries Inc.**
Mexico, Mo. (publicly held)
Paul F. Hummer, chair/pres/CEO
Detrick Refractory Fibers Inc.
This major supplier of refractory shapes sees "very good" sales in 1995 but "slower" for 1996. The company acquired General Refractories, Pittsburgh, Pa., in August 1994. Business outlook: In 1995, we anticipate further growth to higher revenues, and improved productivity and efficiencies to generate enhanced profits.

$144.0 million **American Premier Inc.**
King of Prussia, Pa. (privately held)
Charles H. Gehret, pres.
Premier Refractories & Chemicals Inc., Premier Refractories Canada
American Premier's sales for the first six months of 1995 have been "outstanding." Expect 1996 to be similar to 1994. The company expanded fiber production at Erwin, Tenn.

$110.0 million **Adience Inc.**
Pittsburgh, Pa.(privately held)
Stephen M. Johnson, CEO
BMI Refractories, J. H. France Refractories, Findlay Refractories
Adience is a Division of Alpine Group, New York (Stephen S. Elbaum, CEO). Sales have been excellent, but a slow down is expected toward the end of the year. A new plant was built at Altoona, Pa.

$62.0 million **Resco Products Inc.**
Norristown, Pa. (privately held)
William T. Tredennick, president
Crescent Brick, Resco Products U.K., Pyro Engineering
Resco introduced SUREFLOW™ refractories line. Business outlook: "Should be a good year." There are some soft spots in the over-inventory markets. Resco expects 1996 to be a good year.

$50.0 million* **Aug. Rath Jun. AG**
Vienna, Austria (privately held)
Dr. Ernst Rath, CEO
Rath Deutschland GmbH, Rath Faserformteile GmbH, Rath Hungaria KTF, Rath Keramikfasser GmbH, Rath Perfomance Fibers
Rath is experiencing a "prosperous" year. It expects business to be "rather stable" in 1996.

$42.0 million **Allied Mineral Products Inc.**
Columbus, Ohio (privately held)
Jon K. Taber, pres./chair
North American Processing Co., Matrix Refractories Co.
Allied expects 1995 sales to "be similar to 1994 with increased sales and profits" and 1995 "slowing but not bad." A new R & D facility was completed.

Figure 1-1. *Ceramic Industry's* 1994 listing of the largest refractory producers.[10]

1994, imports were valued at $197 million compared to domestic production at $2 billion and exports in excess $305 million.[11]

The primary consumers of process refractories are the iron and steel, glass, nonferrous metals, cement, and ceramic industries. According to Geiger,[13] the iron and steel industry is by far the largest user of refractories, consuming over 50 percent of the worldwide market. Semler[3] and Longin[14] report similar consumption percentages by the iron and steel industry in the U.S. and U.K. markets, respectively. Consumption by the other four major industries—glass, nonferrous metals, cement, and ceramics—are about 5-10 percent each.[15] Other refractory users include chemical, petroleum, pulp and paper, and mineral processing firms.

Because the iron and steel industry consumes a large and disproportionate share of the total output, improvements in iron and steel production technology directly influence product and technological developments in the refractories industry. For example, the introduction of continuous casting, bottom blowing/stirring to basic oxygen converters, and secondary steelmaking techniques involving stirring and degassing have led to increased tapping temperatures, longer holding times, and greater turbulence in the melt.[15-17] Because the service life of conventional refractories were noticeably reduced under these new conditions, the iron and steelmaking industry created a demand for higher grade and more consistent refractories.

Refractory manufacturers have responded both reactively and in anticipation to their customers' changing needs by developing new products and improving existing ones. Many of these developments were achieved by incorporating new raw materials

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into their refractories. Some new raw materials were developed specifically to meet immediate needs. For example, in 1961, the refractories industry—led by Harbison-Walker Refractories and A. P. Green—developed a very high-purity magnesia, one that substantially improved the performance of magnesite refractories for oxygen-based steelmaking processes.[18,19] Other raw materials, however, existed well before refractory producers recognized their value as a refractory input. For example, tabular alumina, developed in the mid-1930s by Alcoa for aircraft spark plug applications, waited until the 1950s and 1960s before new customer needs stimulated advances in the technology of tabular alumina refractories.[20-23]

The newest raw material to appear in the market is a porous, high alumina aggregate from Alcoa Industrial Chemicals. This material, which the company began marketing in late 1995 under the tradename Plasmal™, is the product of a partnership between Alcoa and a recently-formed joint venture involving Plasma Processing Corporation and Harbison-Walker Minerals.[*] The Plasma Processing joint venture is charged with producing, sizing, and packaging Plasmal™, while Alcoa assumes all sales and marketing responsibilities including distribution, advertising, market and applications development, and after-sales support.

This study is undertaken to support Alcoa in this endeavor by developing lightweight castable refractories with the Plasmal™ aggregate. Castables are a particular type of refractory product, consisting of one or more aggregates held in a matrix material

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[*] Harbison-Walker Minerals and Harbison-Walker Refractories are separate divisions of Indresco.

or binder.[†] By demonstrating that this new aggregate can lead to a new series of castables with properties which satisfy customer needs, we hope to increase demand for this product and accelerate its diffusion into the marketplace.

While the Plasmal™ aggregate may potentially serve the needs of a variety of markets and applications, we selected—in accordance with Alcoa's wishes—the domestic market for lightweight castables for this thesis because it offers an opportunity to exploit the product's unique combination of low density and unusually high refractoriness. As will be explained in more detail in Section 3.0, Plasmal™'s microporous structure and high alumina content make the material relatively lightweight and more resistant to high temperatures than conventional lightweight aggregates such as vermiculite and perlite.

This thesis begins by analyzing the U.S. market for lightweight castables and assessing its needs for new and differentiated products. As much of the recent business literature has advised, product development is not as much about developing new objects or services as it is about fulfilling unsatisfied demand in the market. Upon completion of this study, we begin a series of experiments to formulate castable refractories to meet these needs. We can summarize the objectives of this thesis as follows:

- Research the market for lightweight insulating castables to identify current products and their properties

- Select one or more segments/positions within this market to target new product development

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[†] Castable refractories are described in Section 2.0.

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- Develop new insulating castables using the Plasmal™ aggregate for the targeted segments/positions

Our approach for achieving these objectives is outlined in Section 4.0; our results are presented in Sections 5.0 and 6.0. Before undertaking these topics, we present a brief overview of castable refractories (Section 2.0) and describe the Plasmal™ aggregate and its properties further (Section 3.0).

2.0 Materials Technology of Castable Refractories

A brief overview of castable refractories is presented as background to the marketing and product development studies reported in this thesis. The purpose of this discussion is to provide context to these studies and to introduce technical information and terminology used later in the thesis. Topics discussed in this section include refractory properties, classifications, materials, and production as they pertain to castable refractories.

2.1 Description

Castable refractories, also known as refractory concretes, consist of one or more graded aggregates distributed in a binder or matrix material, usually a hydraulically-setting cement (see Figure 2-1). Castable refractories are furnished as dry, granulated mixtures. They are designed to be mixed with water and formed into specific shapes or monolithic structures at the user's application site. Castables generally are installed by pouring or casting like ordinary concrete but also may be pumped, rammed, tamped, troweled, gunned, or vibrated into place.

Refractory structures built with castable refractories possess functional properties similar to those made with more traditional materials such as refractory bricks and mortar.[24] Castable refractories, however, eliminate the need for skilled bricklayers and reduce the time and cost required to install the refractory structure during both initial build and subsequent replacement.[24,25] In addition, castables: (1) are adaptable to a
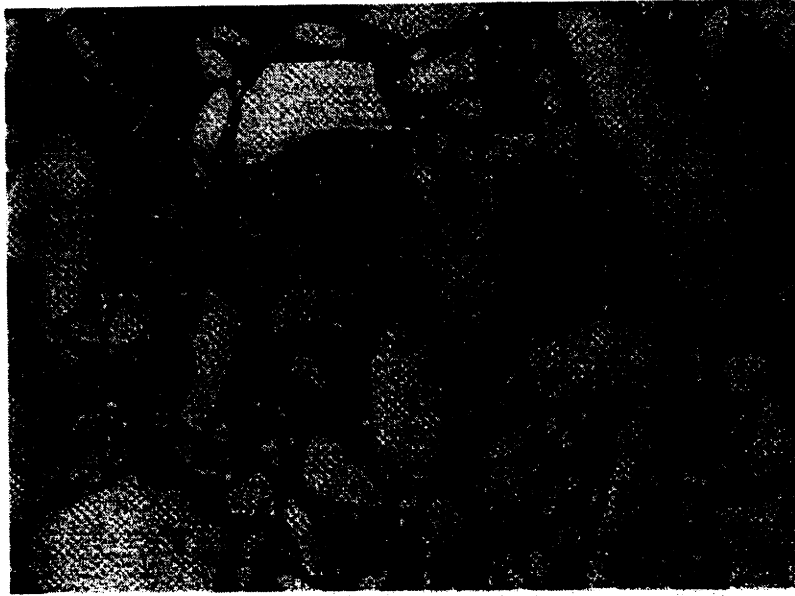
Figure 2-1. Microstructure of a castable refractory showing aggregates (discrete phase) distributed in a cement matrix (continuous phase).[23]

greater variety of configurations, (2) eliminate the need to stock an assortment of standard and special shapes, and (3) form monolithic structures, eliminating joints which provide opportunities for molten solid and slag penetration, and stress concentration.[3,25]

2.2 Properties

The terms *refractory* and *refractories* emphasize the heat-resistance characteristic of these materials. Thermal durability, however, is only one criterion of usefulness. Industrial applications typically require a combination of thermal, mechanical, chemical, and physical properties. Depending on the refractory's expected service environment, these properties may include physical strength, resistance to corrosive attack, and

insulating capability. In addition, flow properties of the uncured refractory slurry are often critical to proper and rapid installation.

The following paragraphs describe the properties of castable refractories, focusing primarily on those relevant to the work reported in this thesis. Because some of these properties are defined by the test methods used to measure them, we refer to standard test procedures where appropriate.

2.2.1 Porosity

Porosity refers to the fraction of empty or void volume in a refractory solid. Refractories are generally porous to some extent, ranging from less than 5 percent for dense products up to 80 percent for highly expanded ones.[24] Voids are often created during production by the following mechanisms: (1) imperfect packing of raw material particles, (2) evaporation and/or decomposition of additives, and (3) shrinkage as raw materials react, melt, or recrystallize.[26]

Manufacturers sometimes deliberately create porosity in a refractory product to reduce its density and increase its insulating capability (see Section 2.2.5). A common method is to incorporate porous raw materials such as vermiculite, perlite, bubble alumina, expanded fireclay, and diatomaceous earth into the refractory.[27] Alternatively, granular organic materials such as ground wood or cork is introduced and subsequently burned out leaving voids.[28]

Porosity data is reported as apparent porosity and true porosity. Apparent porosity, also referred to as open porosity, measures the void space of pores open to the

surface.[29] This measurement is particularly important to process engineers because it characterizes the refractory's resistance to penetration by molten metals, slags, fluxes, and other melts. True porosity, in contrast, is the total porosity of the refractory which includes both open pores and closed pores, the latter being those pores which are enclosed (isolated) in the interior of the refractory.[29]

2.2.2 Bulk Density

The bulk density of a castable refractory is defined by the American Society of Testing and Materials (ASTM) as the ratio of the mass of a cast brick specimen to its nominal or envelope volume excluding any unintentional void defects.[30] This characteristic volume includes the true solid volume and all internal void space whether comprised of closed or open pores. Mass and volume measurements are taken from the cast brick specimen after drying at 230 °F.

Density values are determined primarily by the type and quality of the raw materials used to manufacture the refractory. However, they can be influenced by the size and fit of particles, and the amount of water used to cast the product.[7] As indicated in the previous section, density values can also be manipulated by increasing the degree of porosity in refractory through various means.

In castable refractories, bulk density is typically correlated to other properties such as thermal conductivity and heat capacity.[31,32] In the former case, porosity in the castable accounts for both low density (lightweight) and low thermal conductivity (insulating). This correlation is sufficiently general and common in castables that the

American Concrete Institute use the terms *lightweight castable* and *insulating castable* interchangeably.[33] Thus, bulk density, while an important design parameter itself, also serves to characterize a refractory along other dimensions.

2.2.3 Volume Stability

Volume stability refers to the shrinkage or expansion of a formed castable when fired at high temperatures. Volume stability is measured by permanent linear change, which is defined as the percent dimensional change in length (based on original length) of a refractory specimen free of externally applied stresses, after being subjected to a prescribed heat treatment.[34] Permanent dimensional changes occur as the refractory undergoes mineral inversions, physicochemical reactions, sintering, and related phenomena at firing temperatures.[24]

Neither excessive shrinkage nor excessive expansion is desirable in a refractory material as both tend to impair the strength of refractory structures.[24] However, the former is generally more detrimental to structures as even a few percent shrinkage can lead to "cobblestoning."[35] Expansion, on the other hand, is not necessarily deleterious.[36] In some cases, refractory furnace linings are designed to deliberately expand to seal joints and reduce the risk of molten metal or slag attack.[33,37] Of course, excessive expansion creates internal stresses in the refractory, potentially leading to bowing and even bursting of the structure.[24]

Some refractory materials undergo both expansion and shrinkage during heating. For example, Figure 2-2 shows volume stability data for an alumina fireclay refractory.

After expanding from ambient to 800 °C, the material contracts between 800 and 1200 °C. This is followed by rapid expansion, presumably due to internal gas evolution (bloating), and rapid shrinkage. This behavior is admittedly extreme but illustrates how single measurements may be misleading. For example, data taken only at 1320 °C would suggest that this material undergoes essentially no permanent linear change when in fact it has been very sensitive to temperature changes, cycling between shrinkage and expansion.
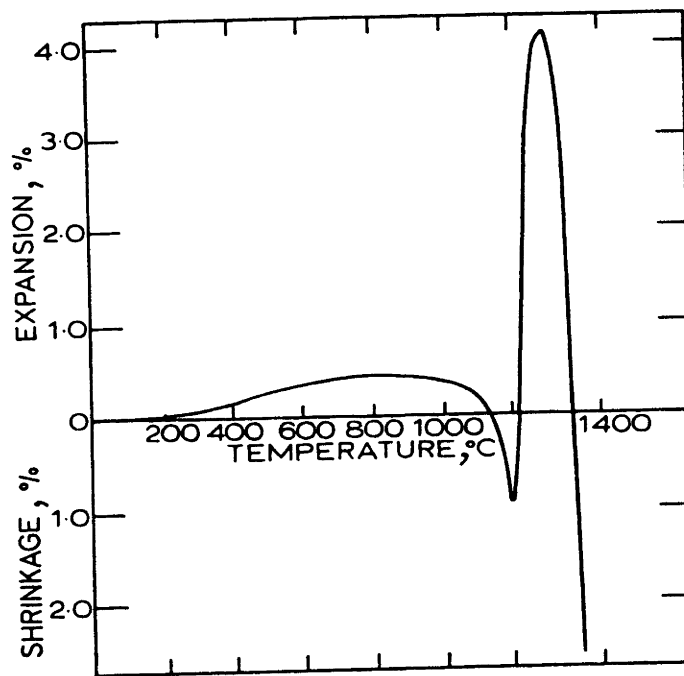
Figure 2-2. Expansion and shrinkage of a medium-alumina fireclay brick.[16]

2.2.4 Modulus of Rupture

Modulus of rupture (MOR) characterizes the cross-bending (i.e., flexural breaking) strength of the material.[31,38] MOR values are determined by applying a stress at the center of a standard-sized bar supported at both ends. The stress is increased at a constant rate until the specimen fails. Procedures for both ambient (cold) or elevated temperature (hot) tests have been established by the American Society for Testing and Materials.[39,40]

Hot MOR data reflects bond strengths at the expected service temperatures and thus indicates the refractory's resistance to spalling, slag attack, and abrasion.[41] However, because these procedures only tests for short term failures, high MOR values do not assure resistance to loads over prolonged periods of time.

Cold MOR data is usually more convenient and less expensive to collect that high temperature data. Refractory suppliers commonly report cold MOR data in product catalogs and other commercial literature. However, these values only indicate bond strengths at room temperature and thus are not necessarily indicative of the material's performance at operating conditions.

2.2.5 Thermal Conductivity

Fourier's law of heat conduction states that the heat flux at a particular point in a material is proportional to the inverse of the temperature gradient at that point. Mathematically, Fourier's law can be expressed as:[42]

$$\mathbf{q} = -\, k\, \nabla T \qquad\qquad\qquad (1)$$

where $\mathbf{q}$ is the heat flux vector and ∇T is the temperature gradient vector. The proportionality constant, k, is defined as the thermal conductivity of the material. The thermal conductivity provides a measure of a material's ability to conduct heat. As indicated by Equation (1), as thermal conductivity increases, so does the heat transfer rate. Materials with high thermal conductivities are good heat conductors while those with low thermal conductivities are good insulators.

Heat transfer in refractories, where some porosity is invariably present, occurs by four mechanisms: heat conduction through the refractory solid, heat conduction and convection through the gas in the pores and other voids, and radiative heat transfer across the pores and other voids.[43-45] Thermal conductivities of refractories thus depend on their mineral compositions, concentration of amorphous material, degree of porosity, size and geometry of pores, and temperature.[46-49] In Section 2.2.2, we noted that porosity plays an important role in reducing thermal conductivity. In particular, as porosity increases, both bulk density and thermal conductivity decrease (see Figure 2-3). This effect is a general one, not limited to refractories. As shown in Table 2-1, the thermal conductivity for a variety of materials decreases as porosity is introduced.

2.3 Classification

The American Society of Testing and Materials (ASTM) organizes castable refractories into five categories based on bulk density, volume stability, lime (CaO) con-

Thermal conductivity, Btu/(hr)(°F)(in)

Fired density, lbs/cu ft
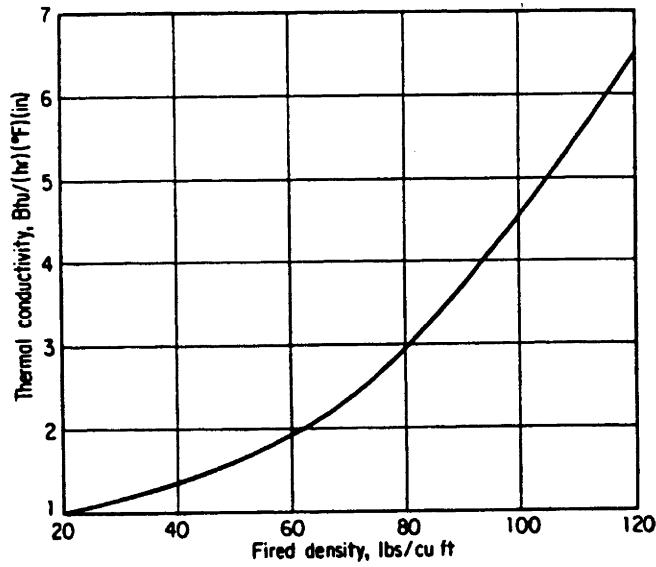
Figure 2-3. Correlation between thermal conductivity and bulk density for insulating castable refractories (Norton[50] using data of Hansen and Livovich[47]).

Table 2-1. Effect of Porosity on Thermal Conductivity of Solid Materials[51]

Substance	Thermal Conductivity (British units)		Porosity (percent)	Form of Porosity
	Solid	Porous		
Calcite	20.5	1.73	49.3	-6 +10 mesh
Steel	400	2.82	41.3	1/8" spheres
Lead	228	2.90	42.0	1/16" spheres
Aluminum	1,600	0.5	98.5	wool
Glass	6.5	0.25	93	silk
Silica (quartz)	62	0.15	95	aerogel
Graphite	2,900	0.14	91	carbon black

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centration, and the presence or absence of a hydraulic-setting cement.[52] These five groups are: (1) Regular Castable Refractories, (2) Low-Cement Castable Refractories, (3) Ultra-Low Cement Castable Refractories, (4) No-Cement Castable Refractories, and (5) Insulating Castable Refractories. Qualifying requirements and additional classifications within these five groups are described in the following paragraphs.

2.3.1 Regular Castable Refractories

Regular castable refractories include alumina and alumino-silicate castables which contain hydraulic-setting cement and have a total lime content greater than 2.5 percent after calcining. These refractories are further classified along strength and volume stability dimensions. Refractories are designated as *normal-strength* if their modulus of rupture exceeds 300 psi, and high-strength if their modulus of rupture exceeds 600 psi. They also take on a letter designation from *A* to *G* based on the volume stability of cast test brick when fired at the temperature prescribed in Table 2-2.

2.3.2 Low-Cement Castable Refractories

Low-cement castable refractories include alumina and alumino-silicate castables which contain hydraulic-setting cement and have a total lime content between 1.0 and 2.5 percent on a calcined basis. No further classifications are made to discriminate among this group of materials.

Table 2-2. ASTM Classifications for Regular Castable Refractories[52]

Class	Permanent Linear Shrinkage *not more than 1. 5% when fired for 5 hours at*
A	2000 °F (1095 °C)
B	2300 °F (1260 °C)
C	2500 °F (1370 °C)
D	2700 °F (1480 °C)
E	2900 °F (1595 °C)
F	3100 °F (1705 °C)
G	3200 °F (1760 °C)

2.3.3 Ultra-Low Cement Castable Refractories

Ultra-low cement castable refractories include alumina and alumino-silicate castables which contain hydraulic-setting cement and have a total lime content between 0.2 and 1.0 percent on a calcined basis. No further classifications are made to discriminate among this group of materials.

2.3.4 No-Cement Castable Refractories

No-cement castable refractories include alumina and alumino-silicate castables which do not contain hydraulic-setting cement and whose bonding agents do not contain lime. A castable may contain up to 0.2 percent of lime on a calcined basis if introduced

into the refractory by its aggregates. No further classifications are made to discriminate among this group of materials.

2.3.5 Insulating Castable Refractories

Insulating castable refractories include those castables which meet the bulk density/volume stability specifications prescribed in Table 2-3. Bulk density is determined from dried cast test brick while volume stability is determined from firings of these specimens.

Table 2-3. ASTM Classifications for Insulating Castable Refractories[52]

Class	Maximum Bulk Density lbs/ft^3 (g/cm^3)	Permanent Linear Shrinkage *not more than 1.5% when fired for 5 hours at*
N	55 (0.88)	1700 °F (925 °C)
O	65 (1.04)	1900 °F (1040 °C)
P	75 (1.20)	2100 °F (1150 °C)
Q	90 (1.44)	2300 °F (1260 °C)
R	95 (1.52)	2500 °F (1370 °C)
S	95 (1.52)	2700 °F (1480 °C)
T	100 (1.60)	2900 °F (1595 °C)
U	105 (1.68)	3000 °F (1650 °C)
V	105 (1.68)	3200 °F (1760 °C)

2.4 Materials

A wide variety of natural minerals and processed synthetics are used to manufacture castable refractories. Aggregates commonly used in lightweight insulating castables and of interest in this thesis include perlite, vermiculite, and fused bubble alumina (hollow spheres of fused alumina). Their properties are described below and summarized in Table 2-4. Other lightweight aggregates include expanded shale, expanded fireclay, and Danish Moler clay.

Among the most important binders are calcium aluminate cements, also referred to as high alumina cements. We discuss their basic features as well as describe various grades within this family of binders. Plasmal™, the refractory raw material of principal interest in this thesis, is discussed later in Section 3.0.

2.4.1 Perlite

Perlite is a siliceous volcanic glass of rhyolitic composition, containing 2-5 percent of water.[53] It appears light gray in color with a pearly luster. It is chemically neutral, having a pH of approximately 7, and generally classified as chemically inert.

One of its distinguishing characteristics is a 4 to 20-fold expansion in volume when quickly heated to elevated temperatures (760 - 1100 °C).[54] The latter feature, which is exploited to manufacture so-called expanded perlite, is caused by the vaporization of hydrated water in the crude (unprocessed) perlite structure. This expansion is extremely rapid, analogous to corn popping, and creates numerous small voids in the solid matrix which account for its low bulk density and other useful properties.

Table 2-4. Typical Properties of Lightweight Aggregates[55-57]

	Perlite	Vermiculite	Bubble Alumina
Chemical Composition, %			
Al_2O_3	12–20	10–18	99
SiO_2	70–75	38–46	0.8
Fe_2O_3	0.7–2.0	5.0–9.0	0.2
TiO_2	0.0–0.3	0.7–1.7	--
CaO	0.6–1.5	0.8–3.8	--
MgO	0.2–0.6	16–24	--
K_2O	3.0–6.0	0.5–6.6	< 0.5
Na_2O	2.7–4.1	0.0–1.7	< 0.5
Bulk density, lbs/ft^3	5–12	3.5–12	34–38
Thermal conductivity, Btu/hr-°F-ft x 10^{-3}	45–65	35–40	300–350
Refractoriness:			
Pyrometric cone equivalent	8–11	N/A	> 38
Maximum temperature, °F	2300–2450	2010	3300–3400

Among the largest global sources of perlite are deposits located in the western United States, principally in New Mexico, California, Colorado, Nevada, and Arizona.[55] Significant international producers are Turkey and Greece; other producers include Japan, Hungary, Italy, Czechoslovakia, Mexico, and Armenia.[58]

2.4.2 Vermiculite

Vermiculite is a platy mineral, consisting mainly of hydrated magnesium silicates

although considerable amounts of aluminum and iron may be present.[59] Vermiculite in its natural state can appear amber, bronze, brown, dark green, or black. Its general composition is given by the following formula.[60]

$$(Mg,Ca)_{0.3}(Mg,Fe,Al)_{3.0}(Al,Si)_4O_{10}(OH)_4 \cdot 8H_2O$$
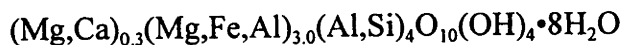
Guner[61] reports the average molecular composition of vermiculite as:

$$22\ MgO \cdot 5Al_2O_3 \cdot Fe_2O_3 \cdot 22SiO_2 \cdot 4OH_2O$$
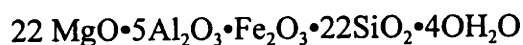
The structure of vermiculite is essentially that of talc with tetrahedral layers separated by oriented water molecules.[62,63] When heated rapidly to 250-300 °C, vermiculite exfoliates or expands at right angles to the basal cleavage into long, wormlike shapes, resulting in a 8 to 12 fold increase in volume.[64] The mechanism of exfoliation involves mechanical separation of the tetrahedral layers as hydrated water is converted to steam and leaves the structure.[65]

Like expanded perlite, expanded vermiculite has higher commercial value than crude or unexfoliated vermiculite. Among the characteristics of the expanded form are low density, chemical inertness, and good thermal and acoustic insulating capability.

2.4.3 Fused Bubble Alumina

Fused bubble alumina is a high-purity alumina (Al_2O_3) material produced by melting calcined alumina in an electric arc furnace and casting it in an air- or steam-pressure stream to yield hollow spheres.[66,67] This process generates a distribution of

sphere diameters which is subsequently screened and separated into suitable size fractions.

Under ideal circumstances, all spheres are received in-tact so that the bulk density is minimized. In practice, however, a portion of the spheres invariably break into smaller fragments even from routine handling and delivery procedures. In addition, when fed into a refractory manufacturing process, additional spheres can fracture, especially in batching and mixing operations (see Section 2.5). Fragmented pieces, of course, have the same bulk density as that of ordinary (dense) fused alumina. Because the interior void space of a hollow sphere is lost when it fragments, these particles do not offer the same ability to reduce density and thermal conductivity as intact spheres when incorporated into a castable.

Advantages that bubble alumina offers include: (1) high refractoriness which yields refractory products capable of hot-face insulation, and (2) very low silica content which makes it suitable for refractories designed for reducing atmospheres.[57,68,69] Its principal disadvantages include lower insulating capability relative to other lightweight aggregates, sensitive bulk density (due to sphere breakage), and high cost (see Table 2-5).[66,69]

2.4.4 Calcium Aluminate Cement

Calcium aluminate cements, also known as high alumina cements, are thermally-resistant, hydraulically-setting cements that are deployed in castable refractories as binding agents. They contain calcium aluminates of low basicity including monocalcium

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aluminate, $CaO \cdot Al_2O_3$, which constitutes the primary phase in the material.[70,71] Other aluminates such as $CaO \cdot 2Al_2O_3$ and $4CaO \cdot 3Al_2O_3 \cdot SO_3$ contribute to strength development of the cement while $12CaO \cdot 7Al_2O_3$, though usually present only in trace amounts, is important in initiating the hydraulic activity of the primary phase $(CaO \cdot Al_2O_3)$.[72,73]

Calcium aluminate cements are generally classified as low purity, intermediate purity, and high purity, depending on their concentrations of alumina, ferric oxide (Fe_2O_3), lime (CaO), and silica (SiO_2).[74,75] Table 2-5 presents the defining specifications for these three grades. Low purity cements contain the lowest levels of alumina and the highest quantities of the other three constituents. The high concentrations of ferric oxide and silica, which act as fluxes in refractory compositions, limit these cements to approximately 2600 °F.[76] In contrast, high-purity cements contain only trace amounts of these impurities, leading to service limits as high as 3400 °F.

The widespread adoption of calcium aluminate cements in castable refractories can be attributed to their excellent refractoriness, high early strength*, excellent refractoriness, high insulating capability, and good thermal shock resistance.[77,78] In addition, solids in these cements are typically very fine, imparting desirable rheological properties to the castable prior to cure which enhance the castable's installation characteristics.[75]

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* *Early strength* refers to the rate at which the cement develops mechanical strength as it cures after water is added. Calcium aluminate cements generally develop high strength within 6 to 24 hours, minimizing downtime of processing units that rely these materials as refractory binders and/or in refractory repair compositions (see reference 73).

Table 2-5. Composition of Calcium Aluminate Cement Grades[73]

| Component | Calcium Aluminate Cement Grade | | |
	Low Purity	Intermediate Purity	High Purity
Al_2O_3	39–50	55–66	70–90
Fe_2O_3	7–16	1–3	0.0–0.4
CaO	35–42	26–36	9–28
SiO_2	4.5–9.0	3.5–6.0	0.0–0.3

2.5 Manufacture

As indicated in the preceding discussion, refractories are manufactured from a relatively broad range of raw materials. Depending on the feedstocks chosen and the type of end product sought, their production may involves some special features. However, the production of castable refractories generally share key common features, making it possible to discuss how castable refractories are manufactured in general. The production process is relatively straightforward, consisting of five primary steps once raw materials are transferred into the manufacturing process: (1) crushing and grinding, (2) screening, (3) batching, (4) mixing, and (5) packaging.[79] A flow diagram illustrating this process and important quality assurance issues is given in Figure 2-4.

Incoming raw materials are first ground and screened to produce desired particles sizes. Particle size distributions can impact the refractory's strength, density, shrinkage at high temperature, and resistance to spalling.[80-82] Some mineral raw materials may require

a drying operation prior to grinding. Quality assurance programs often include regular screen size analyses of materials during both the communition and screening processes.[83]

Specified quantities of each raw material (by material type and particle size fraction) are weighed and delivered to a mixer where these materials are mechanically mixed until a homogeneous solid mixture is achieved. The product is discharged to weighing and packaging stations where suitable lot sizes are prepared and shipped to their destination points.
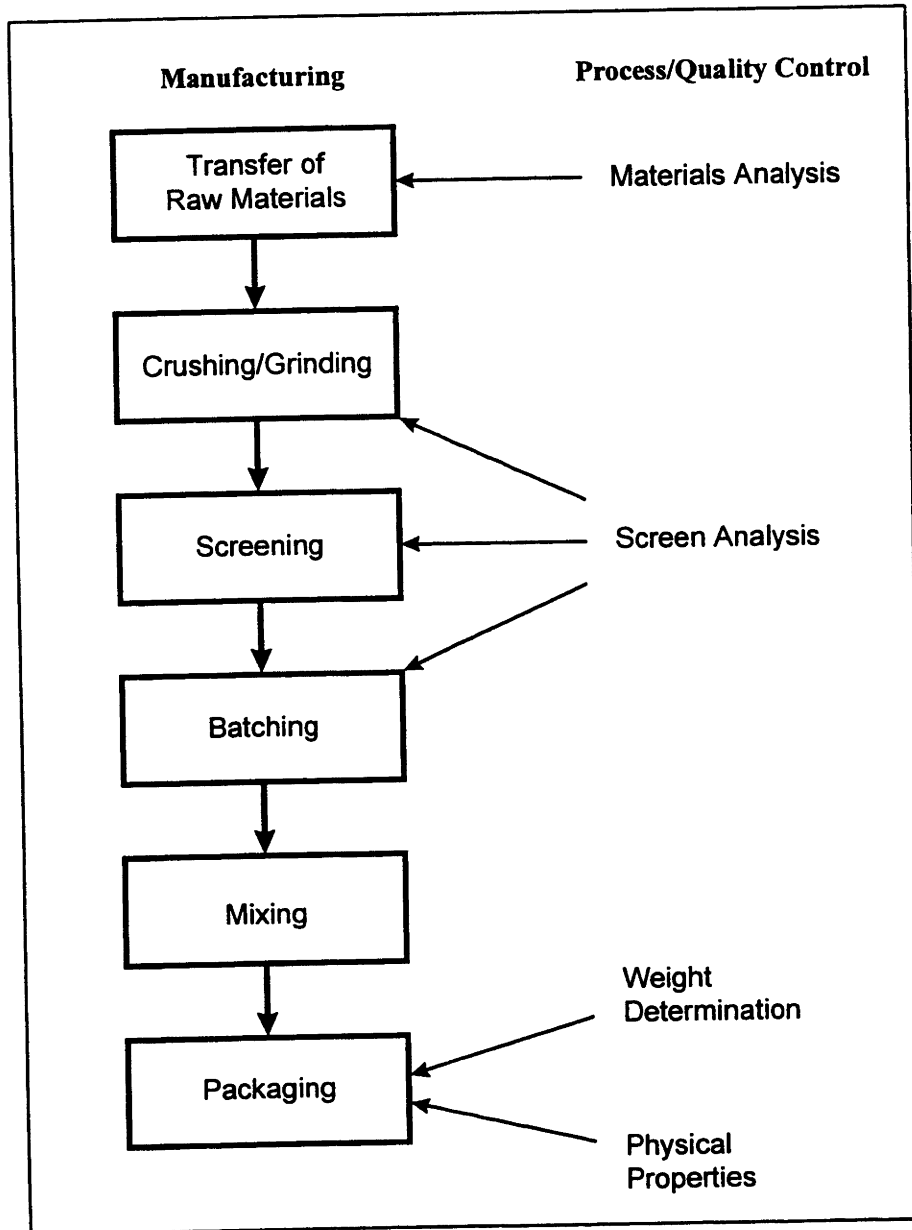
Figure 2-4. Flow diagram of production process used to manufacture
castable refractories.[79]

3.0 Plasmal™ Aggregate

As stated in Section 1.0, the newest product to appear in the refractory raw materials market is the Plasmal™ aggregate. This product, which is being marketed by Alcoa Industrial Chemicals, is a novel synthetic oxide ceramic, characterized by a high alumina content with relatively low thermal conductivity and low density. Its insulating capability is derived in large part to its porosity characteristics—45 to 50% apparent grain porosity with mean pore diameters ranging from 5 to 10 μm (see Figures 3-1 and 3-2).[84] These micropores persist even when the aggregate is ground to -325 mesh (≤ 44 μm) particle size fractions.[85]

Grain bulk densities range from 1.8 to 2.0 g/cm^3 (112 to 125 lbs/ft^3 or pcf). These densities can influence some of the aggregate's other physical properties as indicated in Table 3-1. Thermally, Plasmal™ experiences no weight changes when heated to 2640 °F according to differential thermal analysis/thermal gravimetric analysis. Pyrometric cone equivalent tests indicate that the aggregate can be used up to temperatures slightly above 3362 °F.[86] Thermal expansion data between 75 to 2910 °F (25 to 1600 °C) are given in Figure 3-3.

Chemically, the Plasmal™ aggregate consists predominantly of corundum (α-Al_2O_3)* with magnesium aluminate spinel (MgO•Al_2O_3) inclusions.[87] Also present are lime (CaO), soda (Na_2O), and ferric oxide (Fe_2O_3) in minor concentrations. Table 3-2 reports the chemical composition of the aggregate. X-ray diffraction analysis also de-

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* α-Al_2O_3 is the only thermodynamically stable form of anhydrous alumina. Corundum is generally used to refer to natural mineral occurrences of α-Al_2O_3 in igneous and metamorphic rock (see references 88-90).
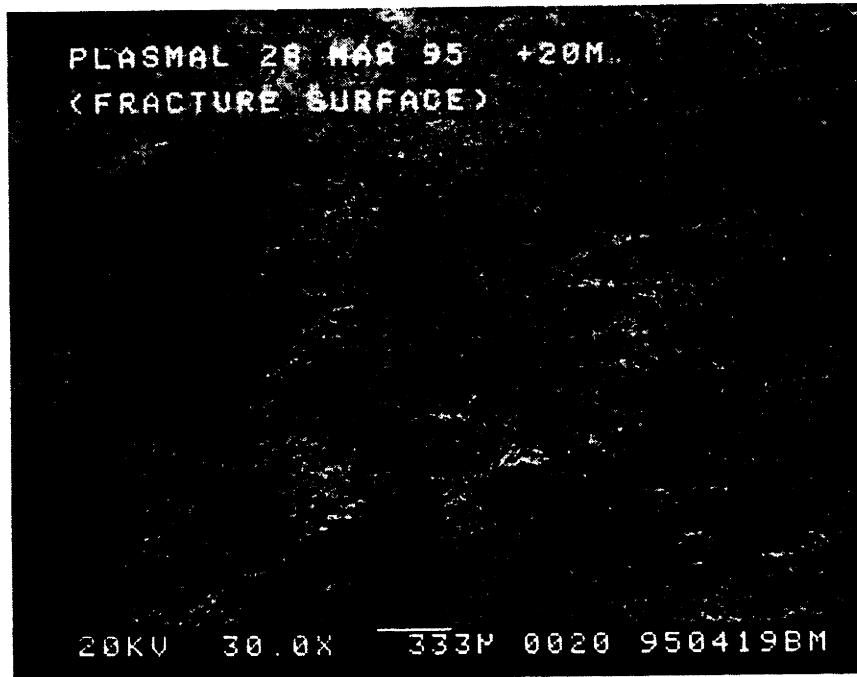
Figure 3-1. Microstructure of Plasmal™ aggregate (fractured surface).
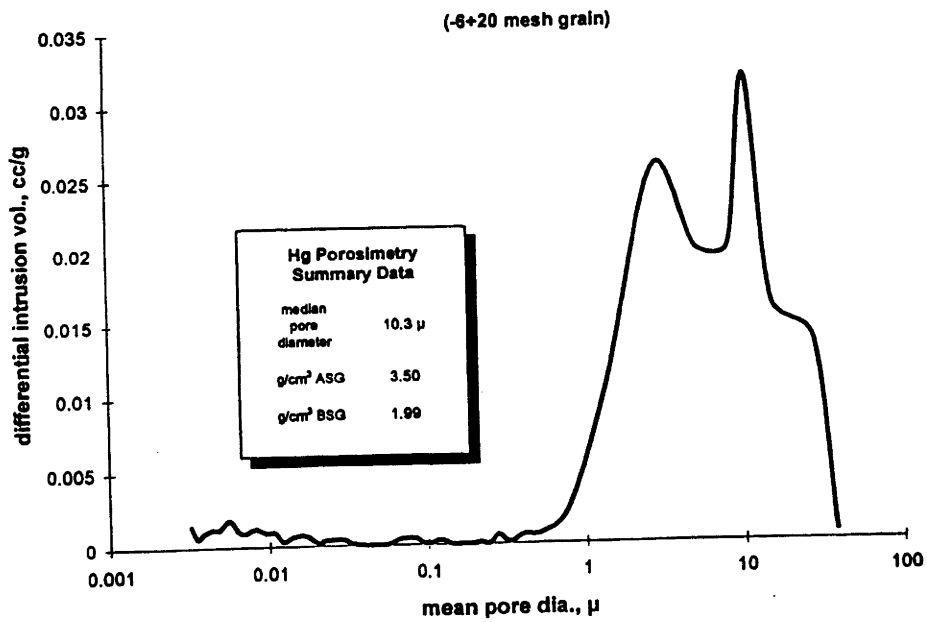
Figure 3-2. Pore size distribution of Plasmal™ aggregate.[87]

tects the presence of β-Al$_2$O$_3$.[91] This metastable form of alumina may be enhancing the refractoriness of the Plasmal™ by reducing the fluxing effect of the alkaline impurities in the material (see Table 3-2).[92]

Plasmal™ offers a genuinely unique combination of chemical, thermal, and physical properties. These properties are achieved by exposing proprietary feedstocks to

Table 3-1. Physical Properties of Plasmal™ Aggregate.[84,91]

	Test Method	Properties with Grain Bulk Density of 112 lbs/ft^3	Properties with Grain Bulk Density of 125 lbs/ft^3
Bulk Density, lbs/ft^3			
Reconstituted (3/4"-fines), loose		84	90
3/8" x 6 mesh, loose		--	72
3/8" x 6 mesh, packed		--	74
Helium Density, g/cm^3		3.75	3.61
Apparent Specific Gravity, g/cm^3	ASTM C 20[93]	3.61	3.57
Bulk Specific Gravity, g/cm^3	ASTM C 20	1.77	1.99
Water Absorption, %	ASTM C 20	28.8	44.2
Apparent Porosity, %	ASTM C 20	50.9	44.2
Pyrometric Cone Equivalent	ASTM C 24[86]	38+ (>3362 °F)	38+ (>3362 °F)
Weight/thermal change, % (ambient to 2640 °F)	DTA/TGA*	0	0

*Differential thermal analysis/thermal gravimetric analysis.

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a high temperature plasma sintering operation.[94] Besides controlling the solid phases formed, this process creates a spheroiding effect on the grain structure.[87] Plasmal™ particles take on convenient spherical shapes when ground which improves the rheological properties of uncured castable refractories. Further details of the process and its effects on the material, unfortunately, are not available. Because the sintering process and its feedstock are both proprietary, its designers at Plasma Processing Corporation have released only limited information.
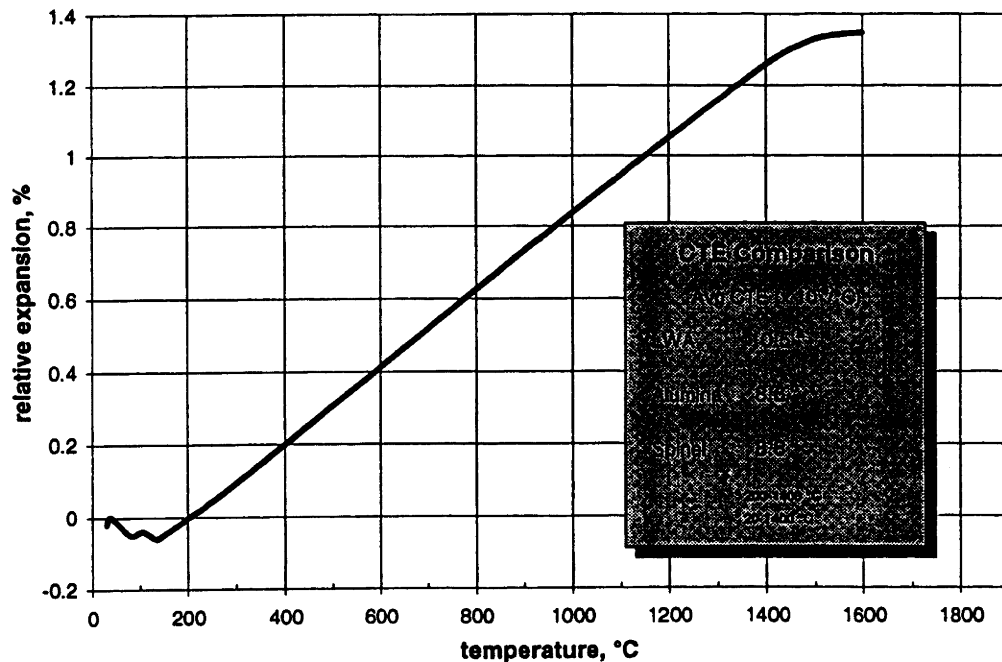
Figure 3-3. Thermal expansion of Plasmal™ aggregate.[87]
(note: Plasmal™ is designated as LWA in the above figure)

Table 3-2. Chemical Composition of Plasmal™ Aggregate[91]

Component	Concentration, %	
	Values with Grain Bulk Density of 1.8 g/cm^3	Values with Grain Bulk Density of 2.0 g/cm^3
Alumina, Al_2O_3	92.6	90.2
Magnesia, MgO	3.36	5.50
Lime, CaO	0.79	1.23
Silica, SiO_2	1.13	1.44
Soda, Na_2O	0.93	0.70
Ferric oxide, Fe_2O_3	0.48	0.48
Manganosite, MnO	0.24	0.21
Potassium oxide, K_2O	0.11	not determined
Titania, TiO_2	0.1	0.16
Tenorite, CuO	0.04	0.05
Chromium oxide, Cr_2O_3	0.04	0.04
Zirconia, ZrO_3	0.03	0.04
Diphosphorus pentaoxide, P_2O_5	0.14	not determined

4.0 Study Approach

The objectives of this thesis, as stated in the Introduction, are: (1) research the market for lightweight insulating castables to identify current products and their properties; (2) select one or more market segments to focus new product development; and (3) develop new insulating castables for the selected market segment(s) using the Plasmal™ aggregate.

To achieve these objectives, we use an approach based largely on product development frameworks proposed by Ulrich and Eppinger[95] and Wheelright and Clark.[96] Our approach, which is represented by the flow diagram in Figure 4-1, consists of the following ten activities:

- Assess existing products

- Identify market needs

- Establish target specifications

- Select refractory system and materials

- Determine density-volume stability properties

- Select refractory formulations

- Assess comparative performance

- Evaluate pilot scale performance

- Confirm full scale performance

- Ramp up production
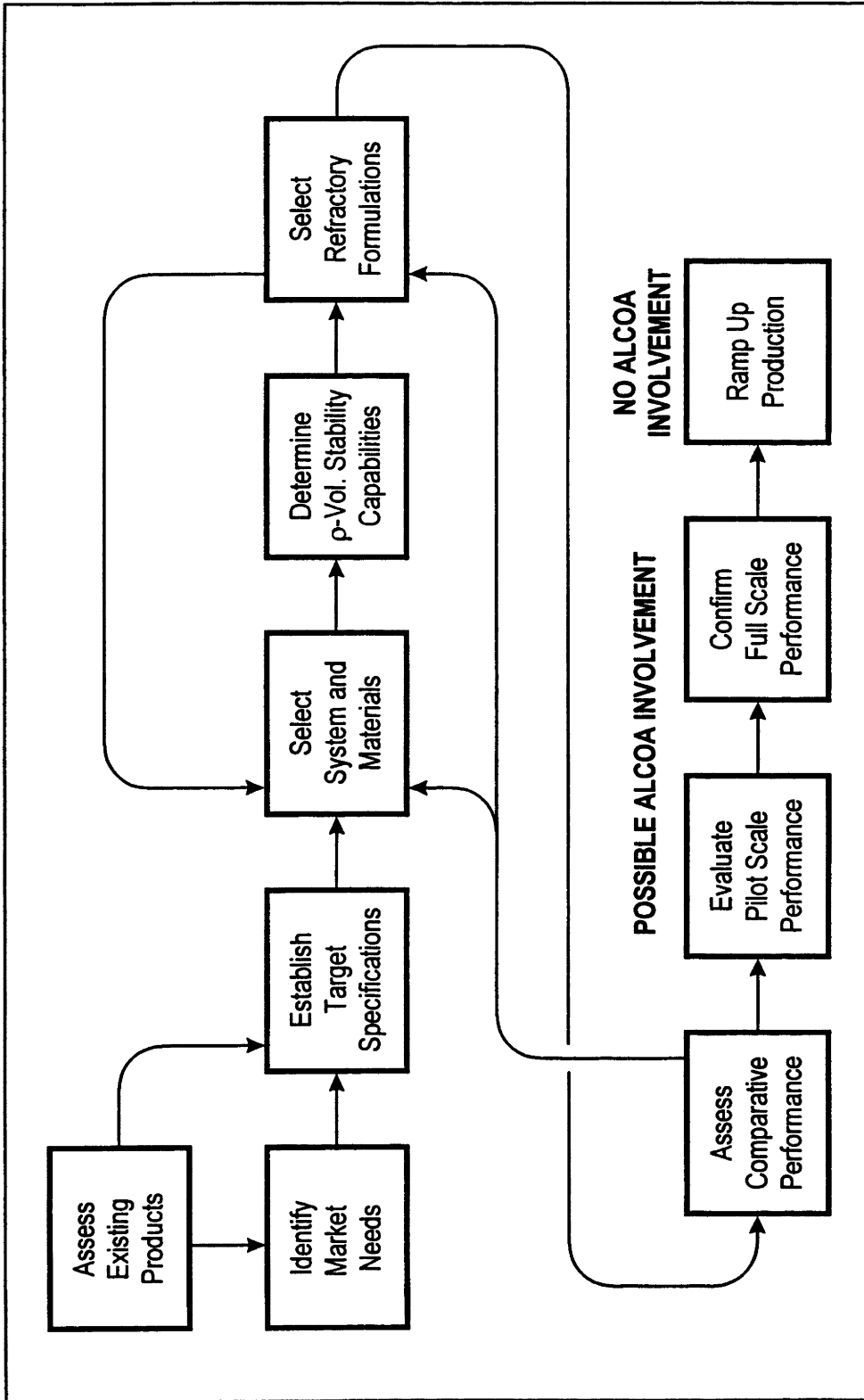
Figure 4-1. Product development process for Plasmal™-based insulating castable.

This thesis undertakes the first five activities, from "assess existing products" to "determine density-volume stability properties." We describe these activities below. The remaining steps are beyond the scope of this thesis. For continuity and information purposes, however, we also describe these activities. Those continuing this work may choose to modify these activities as interim conclusions, business needs, and other factors dictate.

Those familiar with the product development processes of Ulrich/Eppinger and Wheelright/Clark will notice that this approach deviates from theirs. Modifications to their frameworks are necessary because: (1) methods proposed by these two teams of researchers are intended more for discrete goods such as calculators and computer printers than for chemicals and processed materials such as refractories, and (2) those involved in development of the product—namely, MIT and Alcoa—will not manufacture the eventual product; rather, the material formulation will be provided to refractory manufacturers to either produce the castable as designed or use it as a starting point to develop their own formulations.

4.1 Existing Products and Market Needs

We begin the development process by identifying domestic refractory suppliers and their products to characterize the market for lightweight insulating castables. Using perceptual mapping and/or other appropriate marketing techniques, we identify market positions taken by existing products and identify potential opportunities. We will rely heavily on market intelligence from Alcoa's marketing managers to determine which of

these segments or positions are the most attractive as well as vulnerable to new products based on the Plasmal™ aggregate. Of course, at this stage of the project, this assessment will be based on forecasted properties as Plasmal™-based insulating castables have yet to be developed.* These results are reported in Section 5.0.

4.2 Target Specifications

Within our selected market segments/positions, we translate customer needs into target specifications for the refractory product. Specifications are a precise description of what a product has to do.[95] Because insulating castables are defined by their density and volume stability (see Section 2.3.5), we place particular emphasis on these specifications during the initial phase of the product development cycle. Also, as explained in Section 4.4 below, doing so should accelerate the product development process. Target specifications are reported in Section 6.1.

4.3 Refractory System and Raw Materials

We select a castable refractory system and raw materials to experimentally test different product formulations. A typical castable system consists of one or more graded aggregates, a calcium aluminate binder, and various additives to enhance plasticity or other properties. The selected systems and raw materials are discussed in Section 6.3.

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* MacZura and Moody were the first to report on Plasmal™-based castables in October 1995 (see reference 87). However, these products were dense castables, having densities well above 105 lbs/ft³, the maximum allowed for an insulating castable.

4.4 Density-Volume Stability Properties

We synthesize a range of castable products by systematically varying their compositions, and subsequently characterize them by measuring their bulk density and maximum service temperature. Experimental procedures are described in Section 6.2. Density and volume stability capabilities are separated from other performance variables for two reasons. First, as we have already mentioned, these properties define whether a refractory qualifies as a lightweight castable. These properties also provide a useful basis to assess product positioning within the market (see Section 5.1).

Second, subjecting all experimental refractory compositions to full property characterization is wasteful, both in terms of time and personnel/equipment resources. Not every test composition can be expected to qualify as an insulating castable (at least during the initial phases of the product development process). Performing unnecessary tests slows the pace of the product development process and adds unnecessary expense.

Therefore, as indicated in Figure 4-1, we iterate between this step and the previous one above until the desired density-volume stability combination is achieved. We should also note that synthesizing a broad range of Plasmal-based castables is critical at this point because it provides an opportunity to learn how this material behaves in a castable. To date, no lightweight castables have been developed using the Plasmal™ aggregate. We report these results in Section 6.4. Since this is the final activity undertaken as part of this thesis, Alcoa researchers will become involved with the latter portion of this step as a means of transferring the project.

4.5 Refractory Formulations

Products with favorable density-refractoriness properties are selected for further evaluation. Closely-related formulations may be rationalized to reduce testing and eliminate redundant products.

4.6 Comparative Performance

Insulating capability, strength, and other pertinent performance measures of selected refractory compositions are evaluated. Current commercial castables should be tested alongside selected test compositions to assess relative performance.[†] Additional formulation changes may be made to optimize a desired property such as strength or viscosity prior to cure. Of course, density and volume stability should be measured again to ensure they continue to conform to target specifications.

4.7 Pilot Scale and Full Scale Performance

Refractory performance in simulated and actual process environments are conducted to ensure satisfactory performance and resolve any scale-up issues. At this stage, a refractory producer should assume primary responsibility for development from Alcoa. Refractories manufacturers are likely better equipped to handle scale-up issues than a raw materials supplier such as Alcoa. A refractory company and/or refractory user will be required to test the castable with full-size process equipment in simulated and

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[†] Use of standard experiment designs are recommended for these tests (see reference 97).

actual conditions, respectively. Alcoa may choose to participate in these activities in a technical support role. The last step, commercial production, is performed solely by the refractory company as Alcoa is not seeking to integrate forward into the refractories business.

4.8 Production Ramp Up

This activity represents the final phase of converting the proposed product concept into a commercial product. Should the product development process reach this stage, conversion from pilot plant to full-scale production is expected to be assumed by a refractory manufacturer. However, refractory formulations from this thesis may never reach this stage. Rather than producing products as designed here, refractory manufacturers may prefer to use our formulations as a starting point for their own development so that their products are differentiated from their competitors. Production ramp up in this case will involve their own proprietary formulations.

5.0 Marketing Study of Lightweight Insulating Castables

5.1 Industry Characterization

In order to focus our product development efforts, we analyze the domestic market for lightweight insulating castables. We first survey the domestic industry to identify current refractory suppliers. We use several sources to identify companies. Among them include: (1) industry directories published the American Ceramic Society, The Refractories Institute, *Ceramic Industry*, and Aberdeen Group; (2) company representation at the 1995 Ceramic Industry Manufacturing Conference and Expo;[*] (3) referrals from refractory distributors, raw material suppliers, and other refractory manufacturers; (4) patents of recently-developed refractory formulations which list the inventors' company affiliation; (5) journal papers and conference proceedings which list the authors' company affiliation; (6) company advertisements in recent issues of industry periodicals such as the *American Ceramic Society Bulletin*, *Ceramic Industry*, and *Industrial Heating*; and (7) a recent historical monograph on the U.S. refractories industry.[98]

From this survey, we identified 137 refractory suppliers in the United States. The names of these companies are given in Appendix A. In order to substantiate this figure, we consulted government statistics. The latest U.S. Census of Manufacturers, released in 1992, reported that 95 firms manufactured clay refractories[†] and 101 firms manufactured

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[*] Held on October 11-13, 1995, in Pittsburgh, Pennsylvania.
[†] The U.S. Department of Commerce divides the refractories industry into two groups: Clay Refractories under Standard Industrial Classification (SIC) 3255 and Nonclay Refractories under SIC 3297. As their names suggest, clay refractories are defined as those which contain clay while nonclay refractories are those which contain essentially no clay (see references 99-101).

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nonclay refractories.[100,101] Because many firms produce both clay and nonclay refractories, the census data only tells us that between 101 and 196 firms produced refractories in the U.S in 1992. This is admittedly a broad range. The U.S. Department of Commerce, due to confidentiality and other restrictions, could not provide us with more detailed statistics.[102] Because we found no other sources which expanded our list of refractory suppliers, and since the census data at least corroborates our findings, we proceed assuming that this compilation of suppliers satisfactorily represents the domestic industry.[‡]

We reviewed the products offered by these 137 firms as promoted in industry directories and the supplier's sales and technical literature. Of these firms, 24 companies presently supply insulating castables. We define insulating castables according to the ASTM definition given earlier in Section 2.3.5. The names of these firms are given in Table 5-1. Ninety-three of the remaining 137 suppliers do not offer insulating castables as part of their current product line. The remaining 20 firms did not supply us with product information. While these companies agreed to do so, they did not follow through on their commitment even after repeated requests. The results of this survey are summarized in Figure 5-1.

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‡ While we believe that this list of manufacturers likely captures most of the industry, investigation of other sources is recommended. For example, one potentially fruitful source which was not explored in this survey because of time restrictions is refractory consumers.

Table 5-1. Suppliers Offering Insulating Castables in the U.S. Market

Company	Location
BMI Refractories	Carnegie, Pennsylvania
BNZ Materials	Littleton, Colorado
Christy Refractories	St. Louis, Missouri
J. H. France Refractories	Snow Shoe, Pennsylvania
A. P. Green Industries	Mexico, Missouri
Harbison-Walker Refractories	Pittsburgh, Pennsylvania
Matrix Refractories	Chicago, Illinois
Mt. Savage Refractories	Pittsburgh, Pennsylvania
National Refractories & Minerals	Livermore, California
North State Pyrophyllite	Greensboro, North Carolina
Plibrico	Chicago, Illinois
Premier Refractories & Chemcials	King of Prussia, Pennsylvania
Pryor-Giggey Company	Chehalis, Washington
Reno Refractories	Morris, Alabama
Resco Products	Norristown, Pennsylvania
Riverside Refractories	Pell City, Alabama
Saint Gobain/Norton Industrial Ceramics	Worcester, Massachusetts
Skamol	Niagra Falls, New York
Spar	Jacksonville, Alabama
Thermal Ceramics	Augusta, Georgia
TYK Refractories	Clairton, Pennsylvania
United States Refractories	Jacksonville, Florida
Universal Specialties	Pittsburgh, Pennsylvania
Wesco Refractories	Fort Worth, Texas
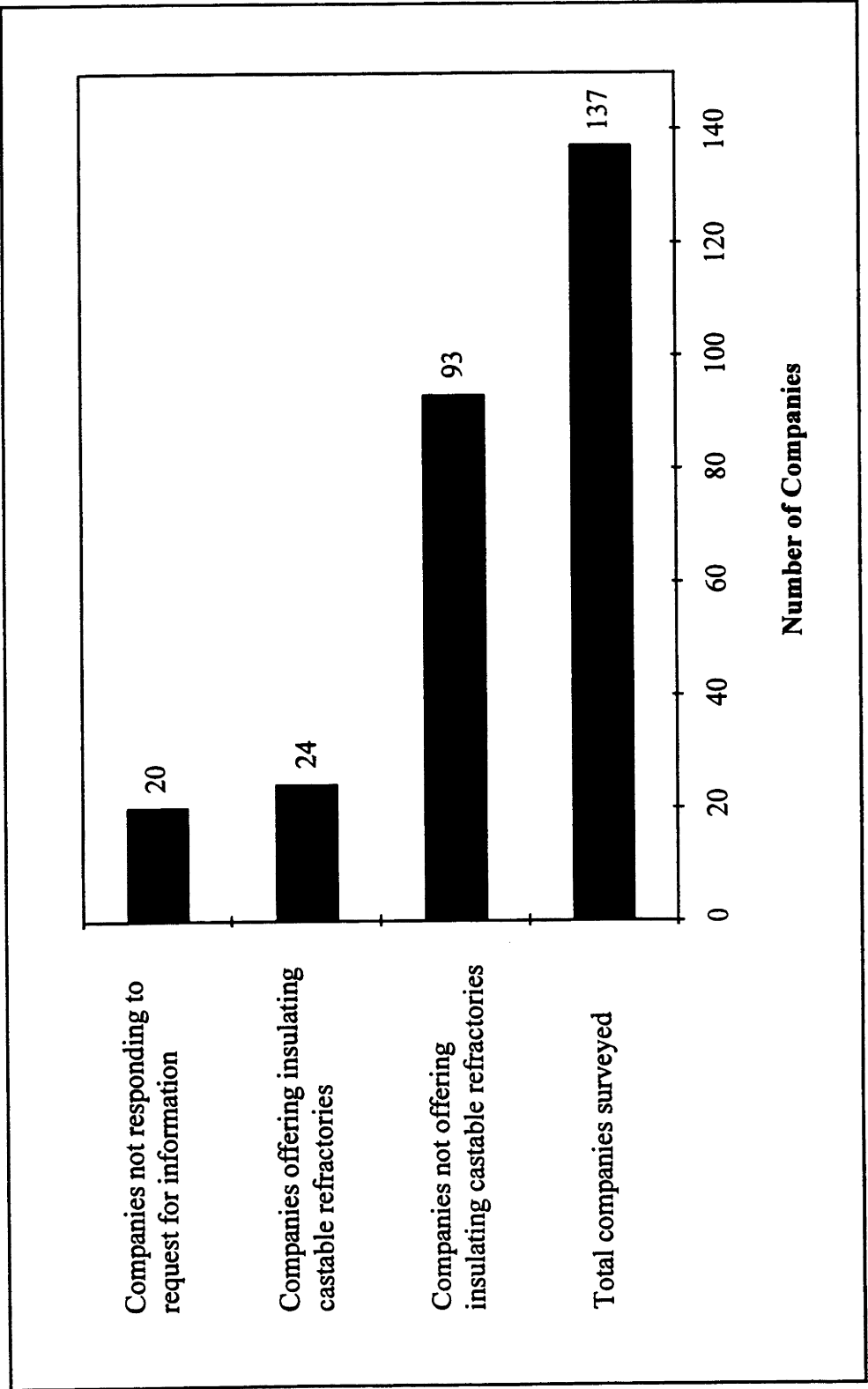
Figure 5-1. Company responses to survey of lightweight insulating castables suppliers.

5.2 Market Definition and Product Analysis

The 24 identified firms currently offer 149 different insulating castable products. Product names are listed in Table 5-2 along with values for bulk density and maximum service temperature. In all cases, density and temperature data is taken directly from the supplier's product literature. Time and resource constraints prevented us from verifying the accuracy of this data by experimentally measuring them or through other means; consequently, we accept them as sufficiently accurate for our purposes. A perceptual mapping diagram illustrating the positioning of these products along density and thermal resistance dimensions is shown in Figure 5-2. As discussed earlier, these two variables are particularly important in assessing these products because they: (1) define whether a product is an insulating castable, [§] (2) partially determine how a product can be used, and (3) are correlated with other properties such as thermal conductivity (or equivalently, insulating capability).

Our mapping diagram illustrates that, in general, as products become more temperature resistant, they also become more dense. This relationship or trend, however, reveals more about the technological and physical limitations of refractory materials than about a particular firm's marketing decisions. Between 1700 and 3500 °F, materials which offer greater thermal stability tend to be denser. Marketing and product decisions, in contrast, are reflected in the positions along this continuum where companies choose to offer products: low density-low temperature resistance versus high density-high

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[§] Suppliers often only list the maximum recommended service temperature for a particular castable without reference to permanent linear change. In these cases, we assume that at this maximum temperature, the permanent linear shrinkage of the castable is less than 1.5 percent.

Table 5-2. Insulating Castable Products

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
A. P. Green Industries	CASTABLE INSULATION NO. 22	53	2200
A. P. Green Industries	GREENCAST 19-L	24	1900
A. P. Green Industries	GREENCAST 45-L	71	2500
A. P. Green Industries	GREENCAST 97-L	89	3300
A. P. Green Industries	GREENKLEEN 45-L	64	2500
A. P. Green Industries	KAST-O-LITE 25	86	2600
A. P. Green Industries	KAST-O-LITE 30	90	3000
A. P. Green Industries	VSL-35	31	2000
A. P. Green Industries	VSL-50	53	2300
BMI Refractories	HYDRALITE 20-40	40	2000
BMI Refractories	HYDRALITE 23-55	55	2300
BMI Refractories	HYDRALITE 23-70	68	2300
BMI Refractories	HYDRALITE 23-90	90	2300
BMI Refractories	HYDRALITE 25-80	82	2500
BMI Refractories	HYDRALITE C23-50	50	2300
BMI Refractories	HYDRALITE C23-60	60	2300

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Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
BMI Refractories	HYDRALITE C24-75	75	2400
BMI Refractories	HYDRALITE C26-85	87	2600
BMI Refractories	HYDRALITE C33-95	95	3300
BNZ Materials	Blazelite 2000 G	64	2100
BNZ Materials	Blazelite 2100	65	2100
BNZ Materials	Blazelite 2300	70	2300
BNZ Materials	Blazelite 2300 LI	61	2300
BNZ Materials	Blazelite 2300 VLI	66	2300
BNZ Materials	Blazelite 2500	78	2500
BNZ Materials	Blazelite 2600 LI	72	2600
Christy Refractories	Morcolite 50R	56	2400
J. H. France Refractories	FRANCOLITE 21	23	1700
J. H. France Refractories	LW HYDRECON 2200LI	53	2200
J. H. France Refractories	LW HYDRECON 29-75	75	2900
J. H. France Refractories	LW HYDRECON 56-2750	60	2750
Harbison-Walker Refractories	H-W® Lighweight Castable Low Iron	57	2200

Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
Harbison-Walker Refractories	H-W® Lighweight Castable 20	˙41	2000
Harbison-Walker Refractories	H-W® Lighweight Castable 22	64	2200
Harbison-Walker Refractories	H-W® Lighweight Castable 25 DS	78	2500
Harbison-Walker Refractories	H-W® Lighweight Castable 26	66	2600
Harbison-Walker Refractories	H-W® Lighweight Castable 33	100	3300
Matrix Refractories	Matrilite 20	53	2000
Matrix Refractories	Matrilite 24AC	77	2450
Matrix Refractories	Matrilite 28AC	79	2800
Mt. Savage Refractories	Delta Crete 22	60	2200
Mt. Savage Refractories	Delta Crete 23-M	80	2300
Mt. Savage Refractories	Delta Crete 25	54	2500
Mt. Savage Refractories	Delta Crete 26	89	2800
Mt. Savage Refractories	Delta Crete 26-M	81	2600
National Refractories & Minerals	FURNALITE	72	2200
National Refractories & Minerals	IRC 20	53	1800
National Refractories & Minerals	IRC 22	56	2250

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Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
National Refractories & Minerals	IRC 24-LI	56	2400
National Refractories & Minerals	IRC 25	87	2500
National Refractories & Minerals	IRC 26-LI	95	2600
National Refractories & Minerals	IRC 29-LI	80	2900
National Refractories & Minerals	MEGOLITE 4-CV	76	2600
National Refractories & Minerals	PUROLITE 30	93	3000
National Refractories & Minerals	VEE BLOCK 35	30	1900
North State Pyrophyllite	LHP 124	60	2100
North State Pyrophyllite	LITE KASTITE 50	73	2000
North State Pyrophyllite	LITE KASTITE 75	93	2500
North State Pyrophyllite	MULLIKAST 80	91	2800
Plibrico	PLICAST AL-REZIST LITE LADLE	65	2300
Plibrico	PLICAST AL-TUFF LWI-20	55	2000
Plibrico	PLICAST AL-TUFF LWI-24	80	2450
Plibrico	PLICAST AL-TUFF LWI-28	80	2800
Plibrico	PLICAST LWI-20	55	2000

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Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
Plibrico	PLICAST LWI-20 TM	60	2000
Plibrico	PLICAST LWI-22	65	2200
Plibrico	PLICAST LWI-24	80	2450
Plibrico	PLICAST LWI-26	80	2600
Plibrico	PLICAST LWI-28	80	2800
Plibrico	PLICAST LWI-606	87	3300
Premier Refractories and Chemicals	ALUGARD™ 75LW	75	2300
Premier Refractories and Chemicals	CER LITE® 18	20	1800
Premier Refractories and Chemicals	CER LITE® 50	52	2000
Premier Refractories and Chemicals	CER LITE® 75	80	2750
Premier Refractories and Chemicals	LINS® 50	50	2300
Premier Refractories and Chemicals	LITE WATE® 35	35	2000
Premier Refractories and Chemicals	LITE WATE® 58	58	2150
Premier Refractories and Chemicals	LITE WATE® 58 LI	66	2300
Premier Refractories and Chemicals	LITE WATE® 70	78	2300
Premier Refractories and Chemicals	LITE WATE® 80 ES	83	2500

Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
Premier Refractories and Chemicals	LITE WATE® 80 ES	83	2500
Pryor-Giggey Company	INSULCAST 25	87	2500
Pryor-Giggey Company	INSULCAST 26	87	2600
Pryor-Giggey Company	INSULCAST 28	89	2800
Pryor-Giggey Company	INSULCAST 30	94	3000
Pryor-Giggey Company	INSULCAST AZS	92	3000
Pryor-Giggey Company	PG LW 80 ES	83	2500
Reno Refractories	RENO LITE CAST 20-55	60	2000
Reno Refractories	RENO LITE CAST 22-70	72	2200
Reno Refractories	RENO LITE CAST 24-60	62	2450
Reno Refractories	RENO LITE CAST 28-80	80	2800
Resco Products	RESCOCAST 3	70	2400
Resco Products	RESCOCAST 3-20R	27	2000
Resco Products	RESCOCAST 3-35	41	2000
Resco Products	RESCOCAST 3-35P	29	2000
Resco Products	RESCOCAST 3-35PC	29	2000

Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
Resco Products	RESCOCAST 3A	67	2400
Resco Products	RESCOCAST 3B	56	2000
Resco Products	RESCOCAST 3E	68	2200
Resco Products	RESCOCAST 4LI	77	2600
Resco Products	RESCOCAST 6	83	2400
Resco Products	RESCOCAST 7	81	2400
Resco Products	RESCOCAST ABC	98	3300
Riverside Refractories	ALALITE 2200	61	2200
Riverside Refractories	ALALITE 2400	64	2400
Saint Gobain/Norton Industrial Ceramics	ALUNDUM® CA-330	80	3300
Saint Gobain/Norton Industrial Ceramics	ALUNDUM® CA-333	100	3300
Skamol	SKAMOCAST Aqualow	47	1742
Skamol	VERMICAST 14-100	62	2012
Skamol	VERMICAST 16-80	48	1832
Spar	SPARLITE 30	93	2950
Spar	SPARLITE 26	83	2600

Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
Spar	SPARLITE 24	78	2400
Spar	SPARLITE 50	50	2300
Spar	SPARLITE 20	58	2000
Spar	SPARLITE 18	43	1800
Thermal Ceramics	Kaolite® 1800	27	1800
Thermal Ceramics	Kaolite® 2000-HS	60	2000
Thermal Ceramics	Kaolite® 2200	60	2200
Thermal Ceramics	Kaolite® 2200-HS	75	2200
Thermal Ceramics	Kaolite® 2300-LI	60	2300
Thermal Ceramics	Kaolite® 2500-HS	85	2500
Thermal Ceramics	Kaolite® 2500-LI	69	2500
Thermal Ceramics	Kaolite® 2600-LI	85	2600
Thermal Ceramics	Kaolite® 2800	86	2800
Thermal Ceramics	Kaolite® 3000-C	75	3000
Thermal Ceramics	Kaolite® 3000-G	95	3000
Thermal Ceramics	Kaolite® 3300	78	3300

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Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
TYK Refractories	Hinomaru Yogyo L.W.C. No. 10	55	1832
TYK Refractories	Hinomaru Yogyo L.W.C. No. 10P	37	1832
TYK Refractories	Hinomaru Yogyo L.W.C. No. 13	75	2372
TYK Refractories	Hinomaru Yogyo L.W.C. No. 14	78	2552
U.S. Refractories	U.S. 70 Lite Wate Insulating Castable	78	2500
U.S. Refractories	U.S. Lite Ware 23 Castable	68	2307
Universal Specialties	UNILITE 2250	59	2200
Universal Specialties	UNILITE 2260	60	2200
Universal Specialties	UNILITE 2560	62	2500
Universal Specialties	UNILITE 2660	56	2600
Universal Specialties	UNILITE 2680	82	2600
Universal Specialties	UNILITE 2880	83	2800
Universal Specialties	UNILITE 2880 AR	87	2400
Universal Specialties	UNILITE 3095	98	3000
Wesco Refractories	WESCOLITE 18	35	1800
Wesco Refractories	WESCOLITE 20	60	2000

Table 5-2. *Continued*

Supplier	Product Name	Bulk Density pcf	Maximum Service Temperature, °F
Wesco Refractories	WESCOLITE 24	82	2400
Wesco Refractories	WESCOLITE 25	82	2500
Wesco Refractories	WESCOLITE 26	85	2600
Wesco Refractories	WESCOLITE 28	100	2800
Wesco Refractories	WESCOLITE 50	51	2300
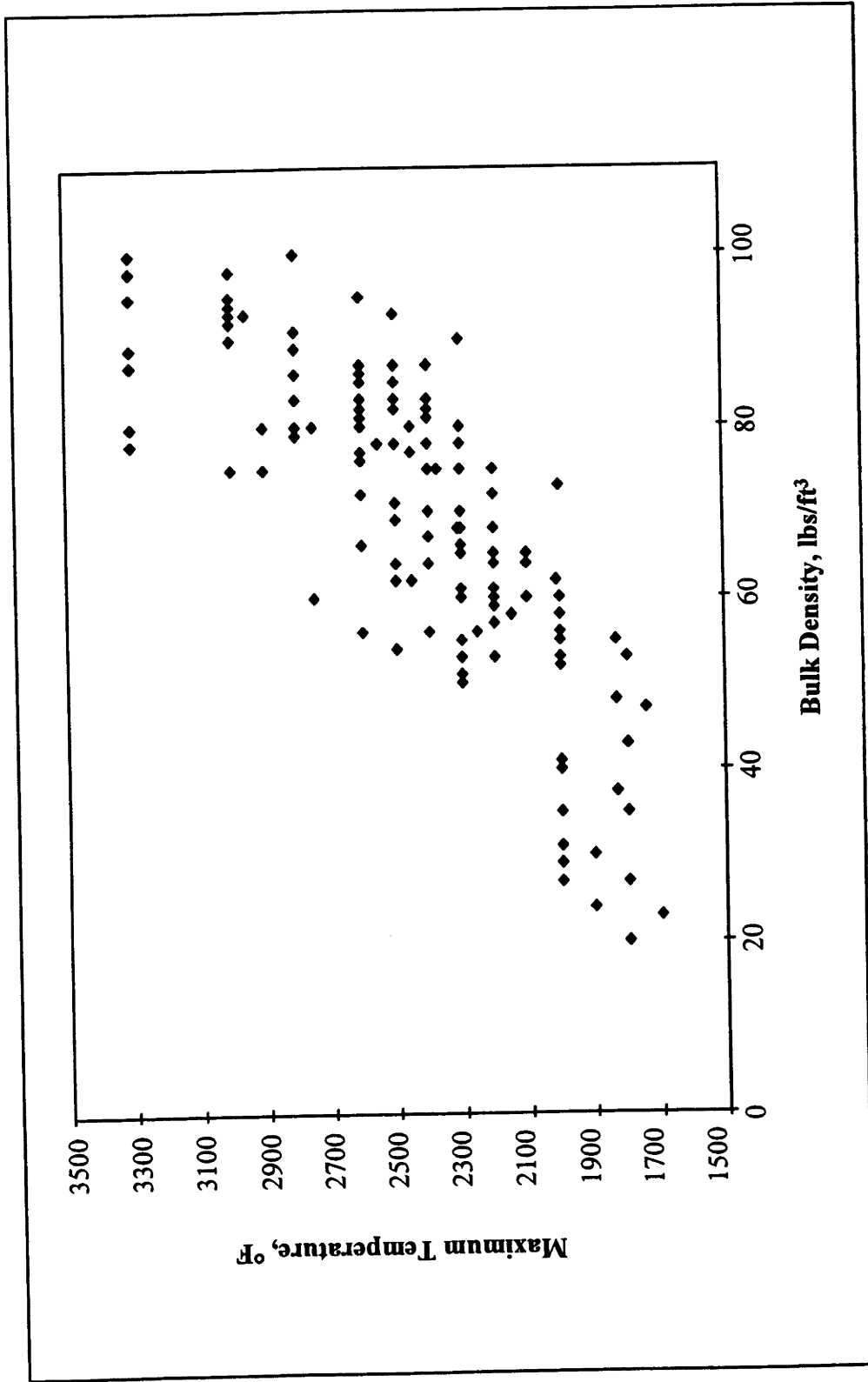
Figure 5-2. Perceptual mapping diagram of lightweight insulating castable refractories.

temperature resistance.

To determine where companies are concentrating their efforts, we investigated which of the nine ASTM insulating castable classifications, N through V, the 149 castable products are capable of meeting.[**] Our results are presented in histogram form in Figure 5-3.[††] Clearly, firms are providing the highest number of products in the 1900-2300 °F range (classes O, P, Q, and R). The number of products offered for classes on either side of this temperature range significantly decrease with the fewest number of products being supplied for the highest temperature ranges (2900 °F and higher).

A second set of marketing and product decisions that suppliers are making can be seen by returning to the perceptual mapping diagram of Figure 5-2. If customers cared solely about minimizing density and maximizing temperature resistance (and optimizing other properties that improve as density-temperature position improves), then only products lying along the northwest boundary of this data set would survive in the market. These products offer the lowest density for any given maximum service temperature, or equivalently, the highest maximum service temperature for any given density. Given that products can compete below this boundary or frontier, we conclude that at least some suppliers have decided to design features into their products that move away them from their optimal density-temperature position.

Ordinarily, we would conduct a customer survey to ascertain these product features and their relative value to customers.[103] This would help us not only understand

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[**] See Table 2-3 on page 30 for qualifying specifications for each class.
[††] Since many product qualify for more than one class, the number of products summed over all classes (351) exceeds the total number of products in our sample (149).
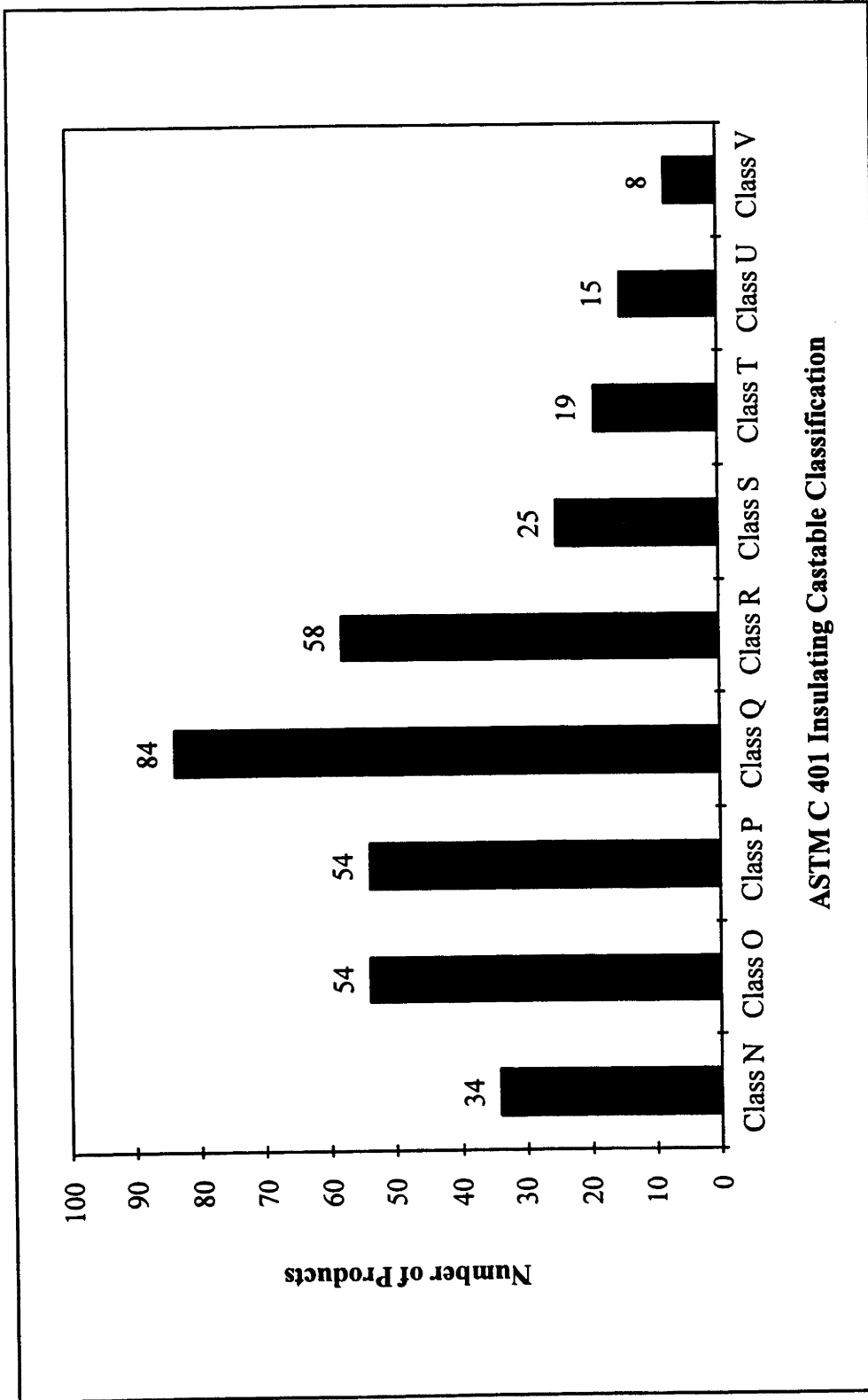
Figure 5-3. Volume stability-temperature analysis of lightweight insulating castable products.

competitor product strategies but also support our own efforts in making these trade-offs and establishing product specifications. Unfortunately, time constraints of this project and its timing relative to Alcoa's activities prevented us from pursuing a survey. We expect that in the future, Alcoa may choose to design and implement such a study.

Without having the benefit of a formal survey, we can speculate that the features refractory manufacturers are trading off with temperature resistance and bulk density include high mechanical strength and low cost. Presumably, their motivation in doing so is to meet customer needs. The degree of movement away from this frontier represents the extent that suppliers are trading off these other properties to design these features into their products. Determining these trade-offs and translating them into product specifications are addressed in Section 6.1.2.

5.3 Market Selection

The ideal market (or ideal position within a market) for new product development is one where market opportunities are attractive and where the innovating firm can leverage its comparative advantages (see Figure 5-4).[104] In the insulating castables market, the most attractive opportunities, according to marketing managers at Alcoa Industrial Chemicals, are in the high-temperature segments, that is, classes T, U, and V.[105] This assessment is based on recent trends in steelmaking and other process industries to increase operating efficiencies by raising process temperatures. These trends translate into needs for insulating castables that are more thermally intractable.

Our findings in the previous section support this viewpoint. ASTM Classes T, U,

Competitive Advantage

	Very strong	Strong	Weak	Very weak
Very attractive	*Favorable Opportunities*			
Attractive				
Unattractive				
Very unattractive				

Market Attractiveness
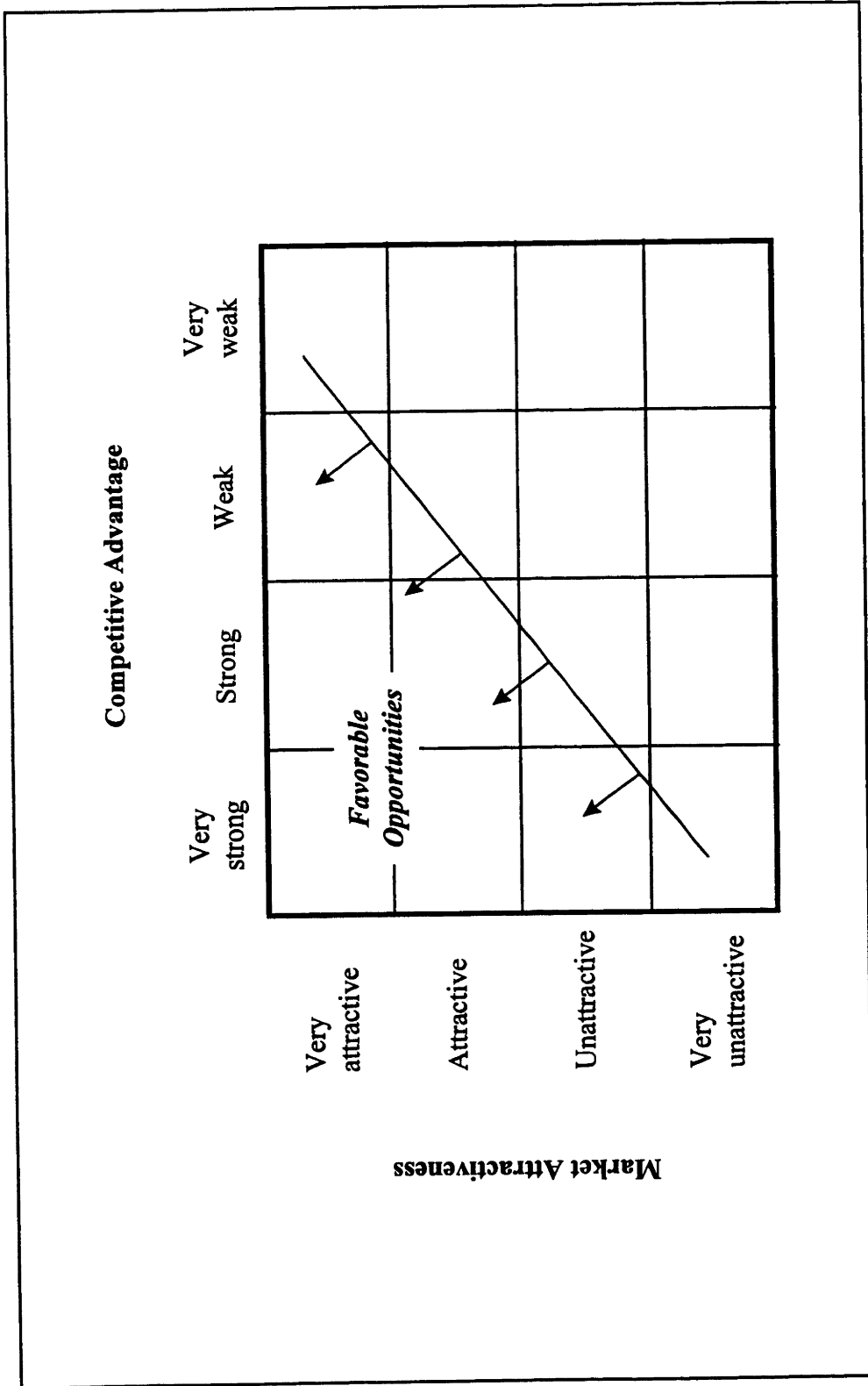
Figure 5-4. Evaluation of market entry opportunities.[104]

and V hold the fewest number of products among all classes (see Figure 5-3). Collectively, they constitute only 10 percent of all insulating castables. Thus, these classes not only represent where customer needs are highest but also where product options are scarcest.

In order to make undertaking a new product development project attractive, however, these classes (i.e., market positions) must also offer opportunities to exploit the comparative advantages of the Plasmal™ aggregate (see Figure 5-4). Fortunately, Plasmal™ is better suited for higher temperatures than lower temperatures. At lower temperatures, castables based on aggregates such as vermiculite or perlite offer lower densities with adequate thermal stability. Furthermore, because these aggregates are among the most inexpensive, these castables may potentially hold a cost advantage. At higher temperatures, on the other hand, vermiculite and perlite do not offer sufficient thermal stability, leaving bubble alumina as Plasmal™'s primary competitor. Because Plasmal™ offers similar densities and refractoriness, its success will likely depend in large part on its ability to develop castables with advantages in cost, thermal conductivity, and other properties. Our goal in this thesis is to develop castables which meet qualification requirements for classes T, U, and V. Once refractories with these properties are attained, the product development process may continue, focusing on refining these castables to achieve the comparative advantages in cost and other characteristics.

6.0 Development of Insulating Refractory Products

6.1 Target Specifications

Target specifications are divided into two groups. The first group addresses objectives for bulk density and maximum service temperature so that the selected ASTM classes—T, U, and V—are met. As discussed in Section 4.0, this portion of the product development process is the subject of this thesis. We discuss these specifications in Section 6.1.1. The second group of specifications addresses cost and additional performance measures within each classification. These are addressed in Section 6.1.2.

6.1.1 Initial Targets

Targets for bulk density and maximum service temperature follow directly from the qualifying requirements of the three classifications. These specifications are given in Table 6-1 (see also Section 2.3).

6.1.2 Cost and Performance Targets

Cost and performance specifications for each of the three classifications (T, U, and V) address additional product characteristics which customers consider when making their purchasing decisions. They must be established such that newly developed products offer a differential or comparative advantage over current products within a given classification. As discussed in Section 5.2, incorporating these features may require trade-offs with other properties.

A critical issue is deciding which characteristics of the refractory product should be specified prior to the start of the product development process. For insulating castables, these characteristics may include mechanical strength, thermal conductivity, and corrosion resistance. Identifying these properties and their specification targets requires: (1) recommendations from those who are sufficiently experienced in the field such that they can set them a priori; (2) results of a marketing research study which empirically identifies these variables and their targets by directly polling markets/customers; or (3) a combination of the previous two options. While this work is necessary, it is beyond the scope of this thesis. Furthermore, besides being unsuitable for publication in this thesis, cost data and pricing strategies are best determined and retained within Alcoa's marketing organization. Therefore, as stated in Section 4.0, we focus this thesis on meeting the first set of specifications.

Table 6-1. Target Specifications for Insulating Castables

Class	Maximum Bulk Density lbs/ft^3 (g/cm^3)	Permanent Linear Shrinkage not more than 1.5% when fired for 5 hours at
T	100 (1.60)	2900 °F (1595 °C)
U	105 (1.68)	3000 °F (1650 °C)
V	105 (1.68)	3200 °F (1760 °C)

6.2 Experimental Procedures and Apparatus

Using facilities at Alcoa's Applications Development Laboratory in Bauxite, Arkansas, we prepared and tested refractory specimens according to the process shown in Figure 6-1. Refractory samples were batched by weighing predetermined quantities of each component on a Mettler Toledo Model 3002 balance with ±0.01 gram resolution. The total weight of all components comprising a particular sample ranged from 300 to 500 grams on a dry basis. Samples were subsequently dry mixed for approximately one minute to ensure a homogeneous granulated mixture.*

The resulting dry mixture was transferred to a 400-ml polyethylene beaker and combined with deionized water to produce a concrete slurry. Because the quantity of water needed to achieve suitable casting properties depends on the components and their respective concentrations in the test sample, this step included not only adding the appropriate amount of water but also first measuring it. Oftentimes, this required an iterative (trial-and-error) process. Slurry consistency was evaluated by qualitative ASTM criteria.[106]

The resultant slurry was manually mixed with a 1-inch stainless steel spatula for 5 minutes and transferred to polyethylene molds. The molds, measuring 2 x 2 x 2-inches, conform to ASTM C 109.[107] Prior to casting the refractory specimens, a thin layer of a vegetable-based release agent was applied on the mold surfaces to facilitate later removal of the specimen. Immediately after casting, specimens were cured by transferring them to

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* Homogeneity is defined on a scale equal to the dimensions of the particle sizes in the mixture.
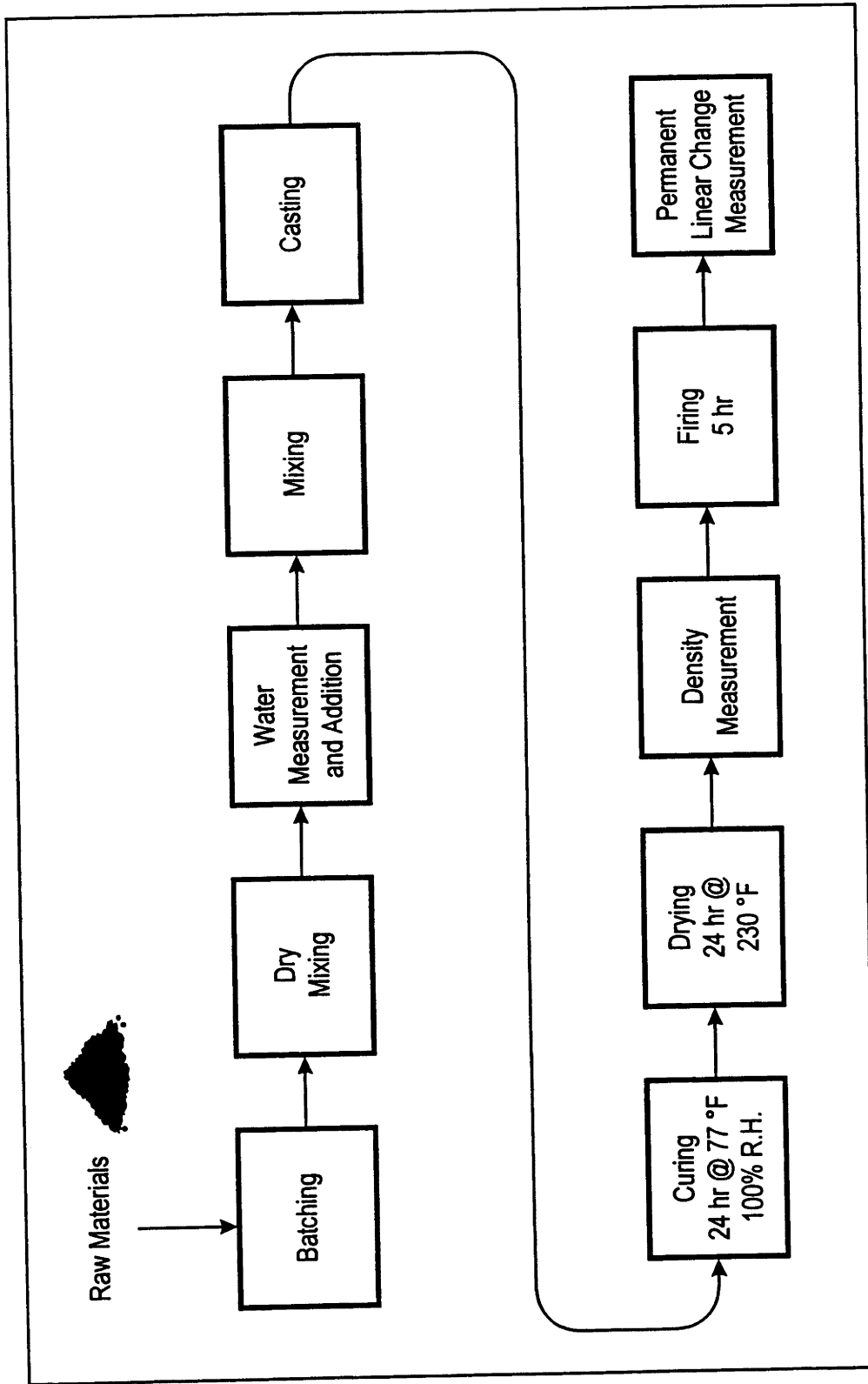
Figure 6-1. Flow diagram of sample preparation and testing process

a sealed humidity chamber at room temperature and 100 percent humidity for a minimum of 20 hours.

The cured specimens were removed from their molds and dried in a Lab Line Imperial V temperature-controlled oven at 230 °F (110 °C) for a minimum of 24 hours. Upon completion of the drying cycle, specimens were weighed and their dimensions recorded. Dimensional measurements were made in three different locations along each of the three axes as shown in Figure 6-2. Bulk density calculations are based on these measurements.

Specimens were fired over calcined alumina plates in an electrically-heated oven at the desired temperature for five hours. Temperature-time profiles showing heating and cooling rates are shown in Figure 6-3. At the end of each firing, the alumina plates were inspected to detect any melting and transfer of components from the refractory specimen. Permanent linear changes were measured along the specimen's x- and y- dimensions (see Figure 6-2). Dimensions along the z-axis were not used to assess volume stability because point-to-point dimension variations along this axis were substantially higher than those along the x- and y-axes. One of the faces perpendicular to the z-axis was open to the atmosphere (i.e., not constrained by a mold surface), increasing its surface roughness and creating these higher point-to-point variations.
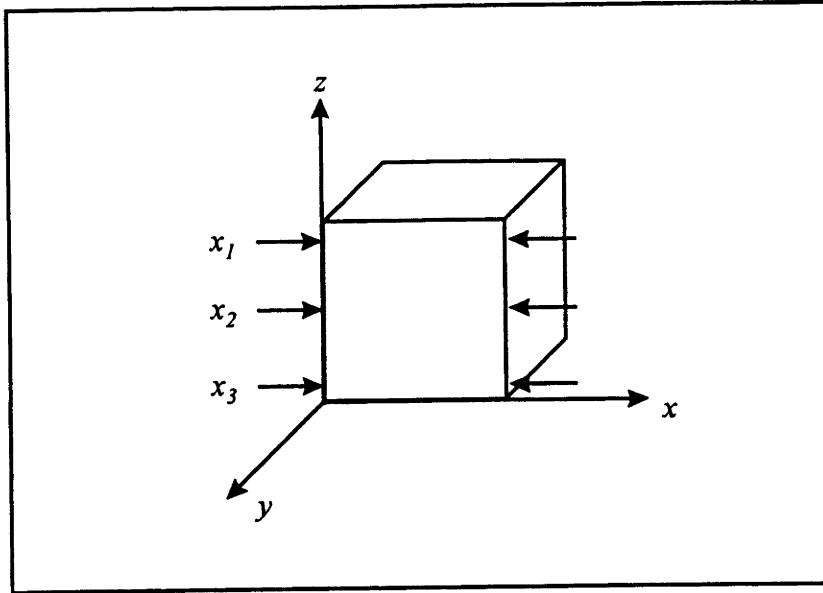
Figure 6-2. Dimensions measured on dried and fired cast specimens
(only x-dimensional measurements shown; y- and z- also measured).
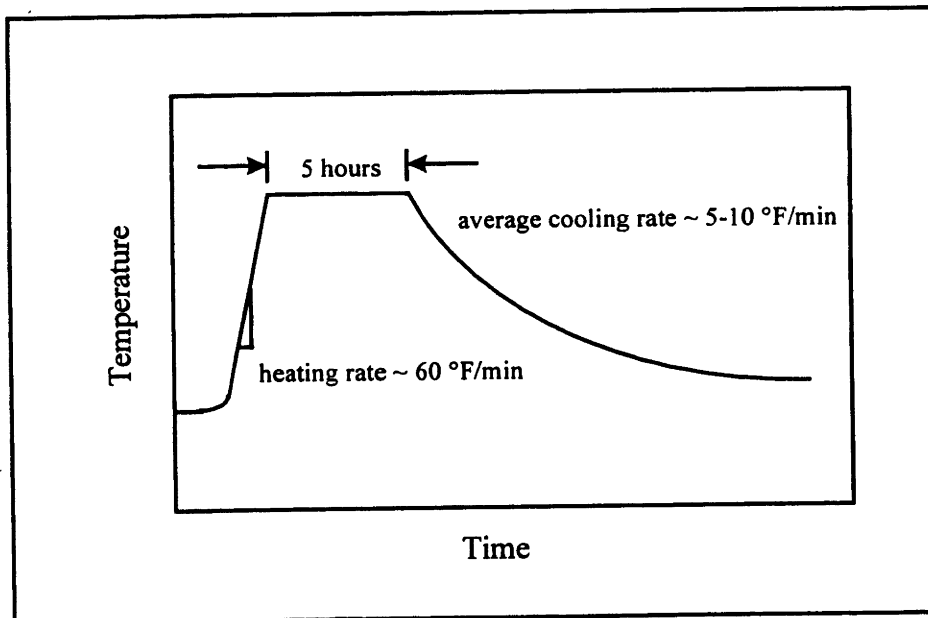
Figure 6-3. Time-temperature profile of specimen firings.

6.3 Refractory System and Raw Materials

6.3.1 Refractory System

The refractory system we use consists of the Plasmal™ aggregate, a lightweight aggregate, plastic kaolin clay, and calcium aluminate cement. In some systems, we exclude the plastic kaolin clay, using only the other three components. Our intent in using the kaolin clay is to vary the cohesiveness and plasticity of the uncured refractory slurry during casting. We use three different lightweight aggregates—perlite, vermiculite, and bubble alumina—and four different calcium aluminate cements of varying purity and alumina content. Test materials are described below.

6.3.2 Plasmal™ Lightweight Alumina Aggregate

Plasmal™ samples arrived in three shipments from Plasma Processing Corporation (Millwood, West Virginia) over the period from October to December 1995. We obtained these samples after they had been ground and screened into the following four size fractions: 3/8 inch x 6 mesh (3.36 - 9.53 mm), 6 x 20 mesh (0.88 - 3.36 mm), 20 x 40 mesh (0.42 - 0.88 mm), and -40 mesh ($\leq$ 0.42 mm). In all cases, we used the Plasmal™ aggregate as received without any further purification, screening, or other processing.

6.3.3 Perlite

We use two expanded perlite products, both supplied by Harborlite Corporation (LaPorte, Texas). These products, identified as IN-8 and UC-216, are both industrial grades of perlite and differ only in their particle size distributions. IN-8 contains much finer (smaller) particle sizes than UC-216 as indicated by Table 6-2. Chemical compositions and other properties for both products are also given in Table 6-2.

6.3.4 Vermiculite

Zonolite® Industrial Vermiculite, supplied by W. R. Grace & Company (Enoree, South Carolina), is a thermally expanded vermiculite intended for industrial applications. In our studies, we use Grade 4 which possesses the finest (smallest) particle size distribution among the Zonolite® variations that W. R. Grace offers. Distribution characteristics are given in Table 6-3 along with chemical composition and physical properties.

6.3.5 Fused Bubble Alumina

Duralum AB Bubbles is a bubble alumina product supplied by Washington Mills Electro Mineral Corporation (Niagara Falls, New York). The product is manufactured by forming gaseous bubbles in molten Bayer alumina, producing hollow spheres of fused alumina. In all cases, we use a 4/F grit ($\leq$ 4.75 mm) size fraction. Chemical analysis and physical properties are given in Table 6-4.

Table 6-2. Chemical and Physical Properties of Harborlite Perlite Products[108,109]

	UC-216	IN-8
Chemical Analysis, %		
SiO_2	77.4	77.4
Al_2O_3	12.8	12.8
K_2O	5.4	5.4
Na_2O	3.1	3.1
CaO	0.5	0.6
Fe_2O_3	0.5	0.5
Physical Characteristics		
Specific Gravity	2.3	2.3
Density, lbs/ft^3		
Loose weight	5.9	--
Tapped weight	6.7	--
Packaged weight	--	2.7 - 3.3
pH Range	6.5 - 7.3	6.5 - 7.3
Particle Size Distribution, % retained		
10, U.S. Mesh Size	10	--
12	15	--
16	30	2.5
20	15	10
30	10	22.5
50	10	40
100	--	15
Pan	10	7.5

Table 6-3. Chemical and Physical Properties of Zonolite® Vermiculite[110]

	Grade 3	Grade 4
Chemical Analysis, %		
SiO_2	38-46	38-46
MgO	16-24	16-24
Al_2O_3	11-16	11-16
Fe_2O_3	8-13	8-13
K_2O	4-6	4-6
CaO	1-3	1-3
TiO_3	1-3	1-3
MnO	0.1-0.2	0.1-0.2
Na_2O	0.1-0.3	0.1-0.3
Physical Characteristics		
Bulk Density, lbs/ft^3	6.7	7.0
Surface Area, m^2/g	8	--
Thermal conductivity, Btu-in/hr-ft^2-°F		
@ 75 °F	0.44	0.44
@ 870 °F	1.16	1.16
Sintering temperature, °F	2100-2200	2100-2200
Fusion temperature, °F	2200-2400	2200-2400
pH (in water)	7.0	7.0
Particle Size Distribution, cumulative% retained		
8, Tyler Mesh	0-10	0
10	0	0
14	0	0-5
28	70-100	0
35	0	0
48	0	60-98
100	0	90-100

Table 6-4. Chemical and Physical Properties of Duralum AB[111]

	Typical Values
Chemical Analysis, %	
Al_2O_3	99.20
SiO_2	0.60
Na_2O	0.15
Fe_2O_3	0.02
CaO	0.01
Physical Characteristics	
Bulk Density, lbs/ft³	35
Thermal conductivity, Btu-in/hr-ft²-°F	4

6.3.6 Calcium Aluminate Cement

We use four commercial calcium aluminate cements as hydraulic binders in our castable refractories. Alcoa Industrial Chemicals (Bauxite, Arkansas) provided two of the four products: CA-14 and CA-25 Calcium Aluminate Cements. Lehigh Portland Cement Company (Allentown, Pennsylvania) provided the other two: Lumnite and Refcon Calcium Aluminate Cements.

CA-14 is a high purity refractory cement which empirically conforms to the formula $CaO \cdot 1.4Al_2O_3$.[112] It consists of approximately 70 percent alumina and can be used up to 3100 °F (1700 °C). Chemical and physical properties are given in Table 6-5.

CA-25, like CA-14, is a high purity hydraulically-setting cement but contains 10

Table 6-5. Chemical and Physical Properties of Alcoa Calcium Aluminate Cements[112,113]

	CA-14	CA-25
Chemical Analysis, %		
Al_2O_3	70.8	80.9
CaO	28.5	18.0
SiO_2	0.5	0.5
Fe_2O_3	0.08	0.07
Na_2O	0.3	0.5
Physical Characteristics		
−325 mesh, wet, %	80	90
Loose Bulk Density, lbs/ft^3	58	56
Pyrometric Cone Equivalent	38	34

percent more alumina. Alcoa offers CA-25 in several variations: Regular Grade, Casting Grade, Long Working Grade, and Gunning Grade. As suggested by their names, these variations are tailored for specific applications and needs. We use Regular Grade exclusively in our experiments and consequently will limit our remarks to this variation.

CA-25 Regular Grade is designed to offer high strength throughout the intermediate and high temperature ranges. It can withstand temperatures up to 3200 °F and above 3400 °F when used with tabular alumina.[113,114] CA-25 conforms to the molar formula $CaO\cdot2.5Al_2O_3$.[113] Alcoa manufactures this cement using pure alumina and lime to minimize fluxing impurities which would otherwise impair its refractoriness. Chemical and physical properties are given in Table 6-5.

Table 6-6. Chemical and Physical Properties of Lehigh Calcium Aluminate Cements[115,116]

	Lumnite	Refcon
Chemical Analysis, %		
Al_2O_3	45.5	56.5
CaO	34.5	34.2
Fe_2O_3	6.0	1.2
SiO_2	8.5	5.0
TiO_2	2.5	2.5
MgO	0.7	0.0
SO_3	0.5	0.3
Physical Characteristics		
Bulk Density, lbs/ft^3	1500	1500
Specific Gravity	3.02	3.02
Specific Surface, m^2/kg	350	350

Refcon and Lumnite are lower priced, less refractory cements. Refcon is an intermediate-purity cement, containing approximately 59 percent alumina, while Lumnite is a low-purity cement, containing only 48 percent alumina. Raw materials for these products are bauxite and lime.[116] Substitution of bauxite for alumina lowers manufacturing costs but increases the concentration of fluxing impurities which reduce these products' refractoriness. Chemical and physical properties of Refcon and Lumnite are given in Table 6-6.

6.3.5 Kaolin Clay

SAPPHIRE, supplied by Kentucky-Tennessee Clay Company (Mayfield, Kentucky), is a secondary kaolin clay. This material, which uses crude clay from Sandersville, Georgia, is processed without beneficiation or additives to yield a pure (100 percent) kaolin.[117] Among the rationale for selecting this product was its fine (small) particle size distribution (see Figure 6-5) which imparts plasticity and high green strength to refractories and ceramics. Its chemical and physical properties are given in Table 6-7.

Table 6-7. Chemical and Physical Properties of SAPPHIRE Kaolin Clay[117,118]

Chemical Analysis, %	
SiO_2	45.50
Al_2O_3	37.70
TiO_2	1.40
Fe_2O_3	0.80
CaO	0.20
K_2O	0.19
MgO	0.15
Na_2O	0.10
L.O.I.	13.50
Physical Characteristics	
Dry Modulus of Rupture, psi	650
Pyrometric Cone Equivalent	33-34
Specific Surface Area, m^2/g	21.0
pH (10% solids)	5.2
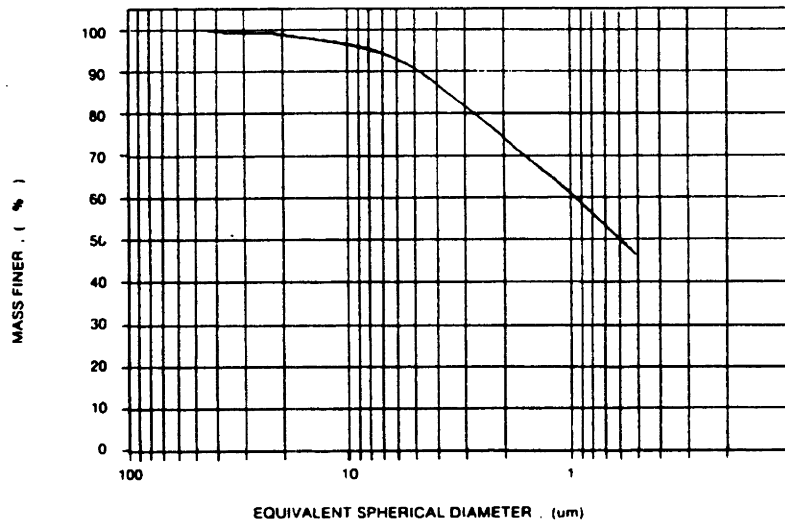
Figure 6-4. Particle size distribution of SAPPHIRE kaolin clay.[118]

6.4 Results and Discussion

6.4.1 Preliminary Screening

We initiated the experimental portion of this study by testing 24 product formulations. In this preliminary screening test, we include three lightweight aggregates (UC-216 perlite, vermiculite, and bubble alumina) and four calcium aluminate cements (Lumnite, Refcon, CA-14, and CA-25). Since these refractories would be the first lightweight insulating castables synthesized with the Plasmal™ aggregate, our intent was to characterize these material systems and acquire an elementary understanding of how these components interacted with each other and affected bulk density and volume

stability. While any product achieving a class T, U, or V qualification would be welcomed, it would be more fortuitous than by design. Test compositions for this initial screening series are given in Table 6-8.

Refractory specimens were prepared and tested in accordance with the procedures described earlier in Section 6.2. Of the 24 different refractory compositions, 5 specimens qualified as Class P castables and 2 specimens qualified as Class Q castables. Bulk density and volume stability values, including the amount of water required to cast the refractory, are shown in Table 6-8. Two of the 5 Class P products contained perlite while the other three contained vermiculite. Both Class Q products used perlite. The remaining 17 compositions failed to qualify for any classification. Among the three lightweight aggregates, only bubble alumina did not yield specimens which met at least one of the insulating castable classifications. Bubble-alumina specimens were generally too dense; the bulk density of 5 of the 8 compositions exceeded 105 lbs/ft^3 (the maximum value allowed for an insulating castable).

6.4.2 Low-Clay Castables

The products tested in the preceding section offer a sufficiently broad range of densities (69 to 122 lbs/ft^3) but lacked dimensional stability at temperatures above 2300 °F. In this series of experiments, we reduce the concentration of kaolin clay from 7 weight percent to a maximum of 3 weight percent. We also limit our calcium aluminate cement options to the higher-purity materials, CA-14 and CA-25. The purpose of these changes is to increase the refractoriness of the castable by reducing component materials

Table 6-8. Refractory Compositions and Test Results of Preliminary Screening Series

No.	Plasmal™* wt %	Kaolin Clay wt %	Lightweight Aggregate Type	wt %	CA Cement Binder Type	wt %	Water wt% dry basis	Bulk Density lbs/ft³	Firing Temperature °F	Permanent Linear Shrinkage[†] mean	std. dev	ASTM Class
PS-1	70	7	UC-216 Perlite	3	Lumnite	20	36	87.7	2300	1.48	0.24	Class Q
PS-2	66	7	UC-216 Perlite	7	Lumnite	20	44	69.9	2100	1.10	0.20	Class P
PS-3	70	7	UC-216 Perlite	3	Refcon	20	35	92.0	2500	3.01	0.95	None
PS-4	66	7	UC-216 Perlite	7	Refcon	20	47	69.3	2100	1.05	0.12	Class P
PS-5	70	7	UC-216 Perlite	3	CA-14	20	34	91.8	2500	3.17	0.70	None
PS-6	66	7	UC-216 Perlite	7	CA-14	20	43	76.9	2300	1.86	0.24	None
PS-7	70	7	UC-216 Perlite	3	CA-25	20	26	102	2900	3.54	0.79	None
PS-8	66	7	UC-216 Perlite	7	CA-25	20	34	82.3	2300	1.23	0.41	Class Q
PS-9	70	7	Vermiculite	3	Lumnite	20	38	87.7	2300	1.91	0.52	None
PS-10	66	7	Vermiculite	7	Lumnite	20	55	70.0	2100	1.29	0.16	Class P
PS-11	70	7	Vermiculite	3	Refcon	20	38	91.8	2500	2.14	0.36	None
PS-12	66	7	Vermiculite	7	Refcon	20	56	69.1	2100	1.37	0.25	Class P
PS-13	70	7	Vermiculite	3	CA-14	20	39	89.8	2300	1.75	0.19	None
PS-14	66	7	Vermiculite	7	CA-14	20	54	70.9	2100	1.29	0.08	Class P
PS-15	70	7	Vermiculite	3	CA-25	20	31	100	2900	3.65	0.27	None

* Plasmal™ consists of the following particle size fractions (relative weight proportion given in parenthesis): 3/8-in x 6 mesh (5:15), 6 x 20 mesh (3:15), 20 x 40 mesh (2:15), and –40 mesh (5:15).
† Negative value for permanent linear shrkinkage indicates volume expansion.

Table 6-8. Continued

No.	Plasmal™ wt %	Kaolin Clay wt %	Lightweight Aggregate		CA Cement Binder		Water wt% dry basis	Bulk Density lbs/ft³	Firing Temperature °F	Permanent Linear Shrinkage		ASTM Class
			Type	wt %	Type	wt %				mean	std. dev	
PS-16	66	7	Vermiculite	7	CA-25	20	48	76.3	2300	1.52	0.41	None
PS-17	70	7	Bubble alumina	3	Lumnite	20	28	105	3083*	4.55	0.68	None
PS-18	66	7	Bubble alumina	7	Refcon	20	27	103	3083*	5.52	2.23	None
PS-19	70	7	Bubble alumina	3	CA-14	20	27	106	3083*	5.63	0.29	None
PS-20	66	7	Bubble alumina	7	CA-14	20	26	104	--	--	--	--
PS-21	70	7	Bubble alumina	3	CA-25	20	19	122	3083*	3.83	0.59	None
PS-22	66	7	Bubble alumina	7	CA-25	20	20	139	2900	1.04	0.47	None

which contribute to glass formation and cause unsatisfactory dimensional stability. We also pursue only perlite and vermiculite compositions, excluding bubble alumina because of the high castable densities it yielded earlier. Test compositions are given in Table 6-9.

Using the same sample preparation and testing procedures as before (see Section 6.2), we obtained the results shown in Table 6-9. Compared to our previous results, these low-clay compositions proved to be more dimensionally stable at high temperatures. Of 17 compositions tested, 3 met Class T, 3 met Classes R and S simultaneously, and 1 met Class Q. Also, over half of these specimens expanded rather than shrunk as would most refractories. In one case, the sample expanded by over 3 percent. Our data, while limited, show that volume expansion is strongly correlated with lower kaolin clay content. Thus, this material system, because it may shrink or expand, potentially gives us the opportunity to control the dimensional stability of the refractory through the Plasmal-to-kaolin ratio.

The bulk density of the refractory varies proportionally with the concentration of lightweight aggregate in the refractory, whether perlite or vermiculite. In Figure 6-6, data from Table 6-9 is plotted along with additional density measurements that we subsequently made. Over the range of lightweight aggregate percentages shown, the dried bulk density of the refractory varies linearly with the lightweight aggregate content. In 4 of the 5 material systems investigated, an increase of 1 weight percent reduces the bulk density by 6.3 lbs/ft^3. The one exception was the perlite/1% kaolin/CA-25 system. A one percent increase in perlite concentration in this case reduces the density by 9.0 lbs/ft^3.

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Table 6-9. Refractory Compositions and Test Results of Low-Clay Series

No.	Plasmal™* wt %	Kaolin Clay wt %	Lightweight Aggregate Type	wt %	CA Cement Binder Type	wt %	Water dry basis wt %	Bulk Density lbs/ft³	Firing Temperature °F	Permanent Linear Shrinkage† mean	std dev	ASTM Class
LC-1	76	1	UC-216 Perlite	3	CA-25	20	24	110	3000	0.33	0.57	None
LC-2	75	1	UC-216 Perlite	4	CA-25	20	28	100	3000	1.68	0.64	None
LC-3	74	1	UC-216 Perlite	5	CA-25	20	33	92.2	2700	-1.48	0.36	Class R/S
LC-4	76	1	Vermiculite	3	CA-25	20	34	98.2	2900	-2.05	0.15	Class T
LC-5	75	1	Vermiculite	4	CA-25	20	39	93.2	2700	-3.36	0.47	Class R/S
LC-6	74	1	Vermiculite	5	CA-25	20	43	85.7	2300	1.25	0.67	Class Q
LC-7	76	3	UC-216 Perlite	1	CA-25	20	21	120	3000	0.69	0.23	None
LC-8	75	3	UC-216 Perlite	2	CA-25	20	23	114	3000	1.74	0.35	None
LC-9	74	3	UC-216 Perlite	3	CA-25	20	25	109	3000	3.23	0.40	None
LC-10	73	3	UC-216 Perlite	4	CA-25	20	29	98.9	2900	1.65	0.31	None
LC-11	76	3	Vermiculite	1	CA-25	20	25	112	3000	0.62	1.93	None
LC-12	75	3	Vermiculite	2	CA-25	20	29	105	3000	1.88	0.10	None
LC-13	74	3	Vermiculite	3	CA-25	20	33	98.2	2900	0.51	0.40	Class T
LC-14	73	3	Vermiculite	4	CA-25	20	39	91.7	2700	-0.26	0.98	Class R/S
LC-15	74	3	Bub. Alumina	3	CA-25	20	20	121	3000	0.13	0.25	None

* Plasmal™ consists of the following particle size fractions (relative weight proportion given in parenthesis): 3/8-in x 6 mesh (5:15), 6 x 20 mesh (3:15), 20 x 40 mesh (2:15), and –40 mesh (5:15).

† Negative value for permanent linear shrkinkage indicates volume expansion.
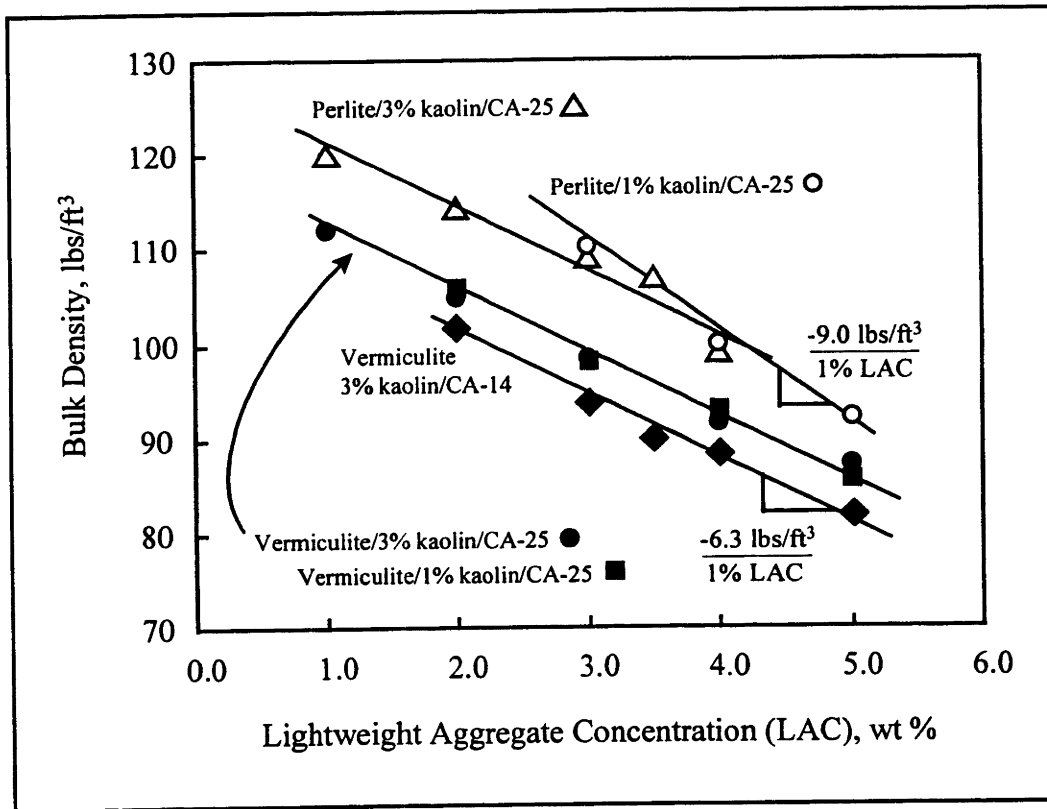
Figure 6-5. Variation of bulk density of low-clay castables with lightweight aggregate concentration (balance of castable percentage is Plasmal™ in size fractions given in Table 6-9).

6.4.3 Clay-Free Refractories

The improvement in dimensional stability that resulted by reducing kaolin clay content naturally led us to investigate refractory formulations which contain no kaolin clay. Again, we use perlite and vermiculite with CA-14 and CA-25 for the reasons given in the last section. We also test IN-8—a perlite product with a finer (smaller) particle

size distribution than the UC-216 product—to aid flow and plasticity properties of the uncured refractory slurry. Specimen compositions are given in Table 6-10.

The temperature stability of these clay-free refractories, in general, increased as extrapolations of the previous data set had predicted. Among the 20 formulations tested, 7 qualified as Class U castables, 2 as Class T castables, 1 as Class R and S simultaneously, and 2 as Class Q. Class V could not be verified owing to temperature limitations of the furnace. Our results are presented in Table 6-10. We also found that the IN-8 aggregate provided satisfactory plasticity to the uncured refractory slurry. In other words, the absence of the kaolin clay in these refractories did not significantly impair their casting characteristics.

Achieving satisfactory plasticity without the kaolin clay component offers the Plasmal™ systems higher flexibility. Flow and cohesive characteristics of the uncured refractory slurry can be controlled by either a lightweight aggregate or a kaolin clay. The lightweight aggregate, however, must consist of sufficiently small particle sizes as in the IN-8 perlite. UC-216 perlite, in constrast, was much more difficult to cast owing to its larger particle sizes. The most common problem during casting was poor cohesion leading to void defects in the castable.

While the refractories produced in this series of products resist temperatures up to 3000 °F (and perhaps higher), they expand considerably more than previous specimens, particularly at temperatures of 2700 °F and higher. While a small degree of expansion often will not present installation difficulties (see Section 2.2.3), some of our test

Table 6-10. Refractory Compositions and Test Results of Clay-Free Series

No.	Plasmal™[*] wt %	Kaolin Clay wt %	Lightweight Aggregate Type	wt %	CA Cement Binder Type	wt %	Water dry basis wt %	Bulk Density lbs/ft³	Firing Temperature °F	Permanent Linear Shrinkage[†] mean	std. dev	ASTM Class
NC-1	76	0	UC-216 Perlite	4	CA-25	20	27	101	3000	0.80	0.52	Class U
NC-2	74	0	UC-216 Perlite	6	CA-25	20	32	91.6	3000	3.01	0.74	None
NC-3	79	0	IN-8 Perlite	1	CA-25	20	24	119	3000	-2.15	0.46	None
NC-4	78	0	IN-8 Perlite	2	CA-25	20	24	114	3000	-1.19	0.22	None
NC-5	77	0	IN-8 Perlite	3	CA-25	20	27	108	3000	1.21	0.70	None
NC-6	76	0	IN-8 Perlite	4	CA-25	20	31	101	3000	2.96	0.97	None
NC-7	78	0	Vermiculite	2	CA-25	20	29	106	3000	-0.90	0.22	None
NC-8	77	0	Vermiculite	3	CA-25	20	33	99.2	2900	-2.37	0.06	Class T
NC-9	76	0	Vermiculite	4	CA-25	20	38	92.3	2700	-4.38	0.20	Class R/S
NC-10	75	0	Vermiculite	5	CA-25	20	43	85.5	2300	0.95	0.53	Class Q
NC-11	79	0	UC-216 Perlite	1	CA-14	20	24	112	3000	-4.29	0.44	None
NC-12	78	0	UC-216 Perlite	2	CA-14	20	24	111	3000	-4.15	0.28	None
NC-13	77	0	UC-216 Perlite	3	CA-14	20	26	104	3000	-3.41	0.43	Class U
NC-14	78	0	IN-8 Perlite	2	CA-14	20	27	108	3000	-3.02	0.33	None
NC-15	77	0	IN-8 Perlite	3	CA-14	20	30	103	3000	-2.08	0.62	Class U

[*] Plasmal™ consists of the following particle size fractions (relative weight proportion given in parenthesis): 3/8-in x 6 mesh (5:15), 6 x 20 mesh (3:15), 20 x 40 mesh (2:15), and -40 mesh (5:15).

[†] Negative value for permanent linear shrinkage indicates volume expansion.

Table 6-10. *Continued*

No.	Plasmal™* Clay wt %	Kaolin Clay wt %	Lightweight Aggregate Type	wt %	CA Cement Binder Type	wt %	Water dry basis wt %	Bulk Density lbs/ft³	Firing Temperature °F	Permanent Linear Shrinkage mean	std. dev	ASTM Class
PS-16	79	0	Vermiculite	1	CA-14	20	27	109	3000	-3.29	0.20	None
PS-17	78	0	Vermiculite	2	CA-14	20	31	103	3000	-3.41	0.24	Class U
PS-18	77	0	Vermiculite	3	CA-14	20	36	95.1	2900	-4.43	0.54	Class T
PS-19	76	0	Vermiculite	4	CA-14	20	41	88.5	2300	0.99	0.36	Class Q

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specimens expanded by as much as 4 percent which likely will be unacceptable for most applications.

The most likely source of this expansion is likely the Plasmal™ aggregate. When Plasmal™ is used in binary refractory systems with CA-25 cement, the expansion is even more significant. While the presence of the lightweight aggregates, which contract at higher temperatures, mitigates the expansion, it does not do so nearly enough. In earlier tests, castables containing 7 percent kaolin clay shrank whenever perlite or vermiculite was also present (see Table 6-8). Thus, while a kaolin clay or similar component may not be required to impart plasticity to the castable, it appears to be needed to prevent the refractory from expanding excessively.

An explicit specification for expansion was not contemplated during this project until these values were observed. We implicitly assumed that the refractories we developed would contract rather than expand like most other commercial refractory systems (ASTM C 401 provides volume stability criteria for shrinkage but not expansion). However, refractories containing the Plasmal™ aggregate are not necessarily confined to contraction. As our results show, expansion is not only a possibility but often the more likely occurrence. Product development specifications for Plasmal™ refractories must therefore go beyond conventional industry standards and include expansion limits.

Like the bulk density of low-clay refractories in the previous section, the density of clay-free castables is a relatively strong function of the concentration of lightweight aggregate, whether perlite or vermiculite. In Figure 6-7, data from Table 6-10 is plotted
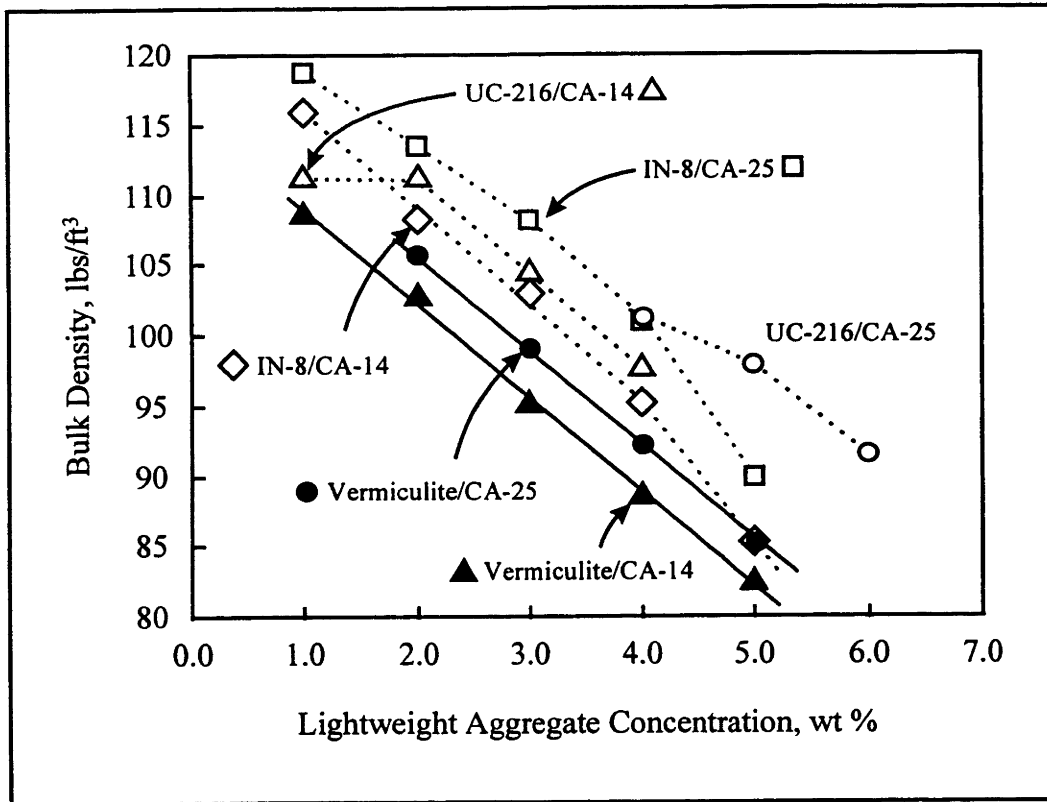
Figure 6-6. Variation of bulk density of clay-free castables with lightweight aggregate concentration (balance of castable percentage is Plasmal™ in size fractions given in Table 6-10).

along with additional density measurements that we made. The density of vermiculite castables vary linearly with vermiculite weight fraction over the range shown. An increase of 1 weight percent reduces the bulk density by 6.7 lbs/ft^3 regardless of whether CA-14 or CA-25 is used.

Perlite castables, in constrast, appear to deviate from this linearity. As shown in Figure 6-6, the density-perlite concentration relationship appear nonlinear, consisting of nonparallel concave functions. Thus, as more perlite is incorporated into the refractory,

its bulk density becomes more sensitive to variations in perlite concentration. One implication of this behavior is stricter process control and quality assurance measures for perlite concentration in the commercial manufacture of perlite-Plasmal™ refractories. Should such perlite-based products reach this stage, we recommend investigating this apparent feature further to determine whether it is simply an artifact of experimental variation in our testing or whether it is a characteristic of this material system.

6.4.4 Effect of Plasmal™ Particle Size Distribution

In all of ours tests so far, we have held the relative proportion of the four Plasmal™ size fractions constant as follows (see Tables 6-8, 6-9, and 6-10):

Size Fraction	Relative Proportion (by weight)
3/8 x 6 mesh	5:15
6 x 20 mesh	3:15
20 x 40 mesh	2:15
-40 mesh	5:15

These proportions are based on a binary refractory composition consisting of Plasmal™ and CA-25 calcium aluminate cement which MacZura and Moody[87] developed earlier for dense castables (>105 lbs/ft^3). In the following experiment, we investigate the effect that more uniformly-sized particles have, if any, on dried bulk density and permanent linear shrinkage.

Two sets of products were synthesized, differing only in Plasmal™ size fractions. The first contained two sizes fractions—20 x 40 and -40 mesh—while the second

contained only -40 mesh. The concentration of vermiculite is varied from 0 to 5 percent. Both product groups contained no clay and 20 percent CA-25 calcium aluminate cement, making them comparable to the vermiculite clay-free refractories in Table 6-10. Compositions for these two product groups are given in Tables 6-11 and 6-12, respectively.

Using the same refractory preparation and test procedures as before, four of the six products qualified as Class Q castables. We determined bulk density values for the remaining two specimens but could not measure their volume stability due to time constraints. Density and permanent linear shrinkage values are shown in Table 6-11 and 6-12 for the two product groups.

Figure 6-7 combines and replots the data from these Tables 6-11 and 6-12 for a side-by-side comparison of the three different particle size distributions. For brevity, we refer to the refractories containing all four size fractions as the baseline distribution. Differences in bulk density and volume stability between the -40 mesh products and the 20x40/-40 mesh products are essentially indistinguishable. However, compared to refractories with the baseline particle size distribution, these two sets of refractories exhibit bulk densities which are 13 to 16 percent lower. This effect is presumably due to less efficient packing from more homogeneously sized particles as discussed by MacZura et al.[82] While time constraints prevented these specimens to be fired at comparable temperatures, it would be interesting to investigate the use of particle size distribution as a means of controlling excessive expansion in Plasmal™-based refractories.

Table 6-11. Refractory Compositions and Test Results of Plasmal™ Dual Size Fraction Series

No.	Plasmal™* wt %	Kaolin Clay wt %	Lightweight Aggregate Type	wt %	CA Cement Binder Type	wt %	Water dry basis wt %	Bulk Density lbs/ft³	Firing Temperature °F	Permanent Linear Shrinkage† mean	std. dev	ASTM Class
DS-1	77	0	Vermiculite	3	CA-25	20	41	85.2	2300	0.91	0.19	Class Q
DS-2	76	0	Vermiculite	4	CA-25	20	45	79.2	2300	0.92	0.17	Class Q
DS-3	75	0	Vermiculite	5	CA-14	20	49	74.5	--	--	--	--

* Plasmal™ consists of the following particle size fractions (relative weight proportion given in parenthesis): 3/8-in x 6 mesh (5:15), 6 x 20 mesh (3:15), 20 x 40 mesh (2:15), and -40 mesh (5:15).
† Negative value for permanent linear shrkinkage indicates volume expansion.

Table 6-12. Refractory Compositions and Test Results of Plasmal™ Single Size Fraction Series

No.	Plasmal™* wt %	Kaolin Clay wt %	Lightweight Aggregate Type	wt %	CA Cement Binder Type	wt %	Water dry basis wt %	Bulk Density lbs/ft³	Firing Temperature °F	Permanent Linear Shrinkage† mean	std. dev	ASTM Class
SS-1	77	0	Vermiculite	3	CA-25	20	41	83.8	2300	0.84	0.10	Class Q
SS-2	76	0	Vermiculite	4	CA-25	20	45	80.3	2300	0.96	0.19	Class Q
SS-3	75	0	Vermiculite	5	CA-14	20	49	74.1	--	--	--	--

* Plasmal™ consists of the following particle size fractions (relative weight proportion given in parenthesis): 3/8-in x 6 mesh (5:15), 6 x 20 mesh (3:15), 20 x 40 mesh (2:15), and -40 mesh (5:15).
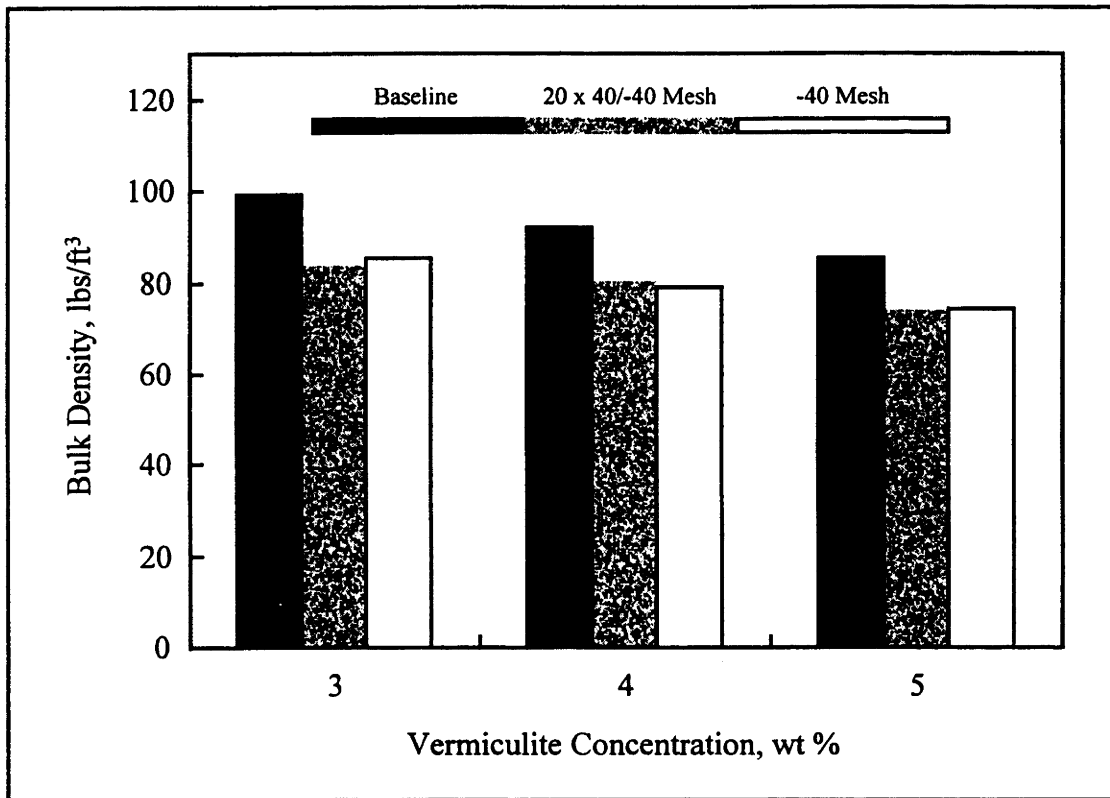† Negative value for permanent linear shrkinkage indicates volume expansion.

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Figure 6-7. Bulk densities of castables containing three different Plasmal™
particle size fractions: (a) baseline distribution (see Table 6-10), (b) only
20 x 40 and -40 mesh, and (c) only -40 mesh

7.0 Conclusions and Recommendations

1. The market for Class T, U, and V insulating castables is the most attractive for targeting Plasmal™-based refractories for the following reasons: (1) production technology trends in refractory-using industries are moving to higher processing temperatures; (2) the refractories industries currently offers the fewest number of products for these segments; and (3) comparative advantages of the Plasmal™ aggregate are best leveraged at temperatures where traditional materials such as perlite and vermiculite cannot compete.

2. Plasmal™-based refractories, when combined with suitable amounts of a lightweight aggregate and calcium aluminate cement, can be designed to meet virtually all of the ASTM insulating castable classifications. In this study, we developed products conforming to Classes P, Q, R, S, T, and U. Class N and O were not pursued because they fell outside the scope of our target market. Compliance with Class V specifications could not be determined owing to temperature limitations of our furnace.

3. Class T castables can be manufactured using 74-76 percent Plasmal™, 3-4 percent vermiculite, 1-3 kaolin clay, and 20 percent high-purity calcium aluminate cement. Permanent linear change of these castables when fired at 2900 °F range from -0.51 percent (shrinkage) to +2.05 percent (expansion). The kaolin clay can be eliminated

from the refractory formulation while retaining Class T qualification and sufficient plasticity. However, expansion at 2900 °F increases to +2.4 percent.

4. While the presence of kaolin clay in the refractory formulation increases the plasticity of the uncured slurry, satisfactory flow and cohesiveness properties can be achieved by selecting a lightweight aggregate product with a suitable particle size distribution. In perlite systems, we found that UC-216 generally required a kaolin clay while IN-8 did not.

5. Class U castables can be manufactured using 76-78 percent Plasmal™, 2-4 percent perlite or vermiculite, and 20 percent high-purity calcium aluminate cement. Permanent linear change of these castables when fired at 3000 °F range from -0.80 percent (shrinkage) to +3.41 percent (expansion).

6. The density of vermiculite castables varied linearly with vermiculite concentration. This relationship persisted even with different calcium aluminate cements and in the presence or absence of kaolin clay. Perlite castables exhibited similar linearity in systems containing 1 or 3 percent kaolin clay. However, in the absence of kaolin clay, our data suggests that the functional relationship between density and perlite concentration becomes nonlinear.

7. We recommend performing a customer survey to determine product attributes that influence the purchasing behavior of refractory users. We also recommend conducting a similar survey to ascertain the product attributes that refractory producers believe their customers are seeking. In this way, both the marketing and product development of the Plasmal™ aggregate and Plasmal™-based refractories can be better focused.

8. We recommend performing paired testing to compare Plasmal™ refractories with competing products in comparable classes (e.g., Class T, U, or V). These tests should include not only bulk density and temperature stability, but also thermal conductivity, mechanical strength and other performance measures. By comparing these materials in side-by-side comparisons, confounding test effects are minimized and relative advantages between these products can be ascertained.

8.0 References

1. Lankford, William T. Jr., Norman L. Samways, Robert F. Craven, and Harold E. McGannon, Eds. *The Making, Shaping and Treating of Steel*, 10th ed. (Pittsburgh: Association of Iron and Steel Engineers, 1985), 1-35.

2. Carniglia, Stephen C., and Gordon L. Barna. *Handbook of Industrial Refractories Technology: Principles, Types, Properties and Applications* (Park Ridge, NJ: Noyes Publications, 1992), 2.

3. Semler, Charles E. *Refractories in the Iron and Steel Industry*. Presentation to Alcoa Industrial Chemicals, Pittsburgh, PA, May 23-24, 1995.

4. Krause, Corrine Azen. *Refractories: The Hidden Industry. A History of Refractories in the United States, 1860 to 1985* (Westerville, OH: American Ceramic Society, 1987), 1-3.

5. Hasselman, D. P. H. Unified theory of thermal shock fracture initiation and crack propagation in brittle ceramics. *J. Amer. Cer. Soc.* **1969** *52*(11), 600-604.

6. Norton, F. H. *Elements of Ceramics*, 2d ed. (Reading, MA: Addison-Wesley, 1974), 282-292.

7. O'Driscoll, Mike, and Karen Harries-Rees. An introduction to refractories. O'Driscoll, M. J., and J. B. Griffiths, Eds. *Raw Materials for the Refractories Industry*, 3d ed. (London: Metal Bulletin, 1993), 7-8.

8. Nielsen, Ralph H. Preparation of refractory metals. Hausner, Henry H., and Melvin G. Bowman, Eds. *Fundamentals of Refractory Compounds* (New York: Plenum Press, 1968), 185-201.

9. Eck, R. Refractory metals and alloys. Bullock, E., R. Brunetaud, J. F. Conde, S. R. Keown, and S. F. Pugh, Eds. *Research and Development of High Temperature Materials for Industry* (London: Elsevier Applied Science, 1989), 79-88.

10. Anonymous. Giants in refractories. *Ceramic Industry* **1995** *145*(3), 47-49.

11. U.S. Department of Commerce. *Refractories: Current Industrial Report*, MA32C. Washington, DC: U.S. Department of Commerce, Bureau of the Census, 1994.

12. Harries-Rees, Karen. Refractory majors: plagued by overcapacity. O'Driscoll, M. J., and J. B. Griffiths, Eds. *Raw Materials for the Refractories Industry*, 3d ed. (London: Metal Bulletin, 1993), 9-21.

13. Geiger, Greg. Testing and standardization in steel-plant refractories. *Amer. Cer. Soc. Bull.* **1992** *71*(7), 1084-1095.

14. Longin, H. Trends in the European refractories industry. *Amer. Cer. Soc. Bull.* **1988** *67*(7), 1161-1162.

15. Lee, William E., and W. Mark Rainforth. *Ceramic Microstructures: Property Control by Processing* (London: Chapman and Hall, 1994), 452.

16. Semler, Charles E., and Laurel M. Sheppard. Needs and concerns of the U.S. Refractories Industry. *Amer. Cer. Soc. Bull.* **1988** *67*(7), 1158-1160.

17. Irving, W. R. *Continuous Casting of Steel* (London: The Institute of Materials, 1993), 7-33.

18. Thomas, Dana. Uncommon clay. *Barron's* **1966** (Feb. 1), 7.

19. Anonymous. High purity magnesia. *The Iron Age* **1962** *189*(Feb. 1), 57.

20. Krause, 154.

21. Anonymous. *Building on Our Strengths: The Story of Alcoa Industrial Chemicals.* Pittsburgh: Alcoa Industrial Chemicals, 1995.

22. MacZura, George. Production processes, properties, and applications for tabular alumina refractory aggregates. Hart, L. D., Ed. *Alumina Chemicals: Science and Technology Handbook* (Westerville, OH: American Ceramic Society, 1990), 109-170.

23. Lankard, David R. Evolution of monolithic refractory technology in the United States. Fisher, Robert E., Ed. *New Developments in Monolithic Refractories. Advances in Ceramics,* Vol. 13 (Columbus, OH: American Ceramic Society, 1985), 46-66.

24. Shaw, Kenneth. *Refractories and Their Uses* (New York: Wiley, 1972), 4-31.

25. Bakker, W. T. *Properties of Refractory Concretes,* SP-57 (Detroit: American Concrete Institute, 1978), 11-52.

26. Carniglia and Barna, 217.

27. Norton, F. H. *Refractories,* 4th ed. (New York: McGraw-Hill, 1968), 143-144.

28. Clements, J. F. Characteristics of refractory insulating materials. *Trans. Brit. Cer. Soc.* **1966** *65*, 479-496.

29. Kingery, W. D., H. K. Bowen, and D. R. Uhlmann. *Introduction to Ceramics*, 2d. ed. (New York: Wiley, 1976), 520.

30. Committee C-8 on Refractories. *Standard Test Methods for Size and Bulk Density of Refractory Firebrick and Insulating Firebrick*, ASTM C 134. Philadelphia: American Society of Testing and Materials, 1988.

31. Sutton, J. P., and S. W. Thrower, Eds. *Modern Refractory Practice*, 5th ed. (Pittsburgh: Harbison-Walker Refractories, 1992), PR-2 - PR-5.

32. Chesters, J. H. *Refractories: Production and Properties* (London: Iron and Steel Institute, 1973), 428-430.

33. Fowler, Timothy J. Ed. *State-of-the-Art Report: Refractory Plastics and Ramming Mixes*, ACI 547.1R-89 (Detroit: American Concrete Institute, 1989), 7.

34. Committee C-8 on Refractories. *Standard Terminology Relating to Refractories*, ASTM C 71. Philadelphia: American Society for Testing and Materials, 1993.

35. Chester, 155.

36. Chester, 297-298.

37. Budnikov, P. P. *The Technology of Ceramics and Refractories* (Cambridge: MIT Press, 1964), 120-121.

38. O'Bannon, Loran S. *Dictionary of Ceramic Science and Engineering* (New York: Plenum Press, 1984),169.

39. Committee C-8 on Refractories. *Standard Test Methods for Cold Crushing Strength and Modulus of Rupture*, ASTM C 133. Philadelphia: American Society for Testing and Materials, 1991.

40. Committee C-8 on Refractories. *Standard Test Methods for Modulus of Rupture of Refractory Materials at Elevated Temperature*, ASTM C 583. Philadelphia: American Society for Testing and Materials, 1980.

41. Hancock, J. D. *Practical Refractories* (West Yorkshire, England: Cartworth Industries), 57-58.

42. Bird, R. Byron, Warren E. Stewart, and Edwin N. Lightfoot. *Transport Phenomena* (New York: Wiley, 1960), 245.

43. Loeb, Arthur L. Thermal conductivity: VIII, A theory of thermal conductivity of porous materials. *J. Amer. Cer. Soc.* **1954** *37*(2), 96-99.

44. Young, R. C., F. J. Harwig, and C. L. Norton. Effect of various atmospheres on thermal conductance of refractories. *J. Amer. Cer. Soc.* **1964** *47*(5), 205-210.

45. Lee, D. W., and W. D. Kingery. Radiative heat transfer and thermal conductivity of ceramic oxides. *J. Amer. Cer. Soc.* **1960** *43*(11), 594-607.

46. Ruh, Edwin, and Albert L. Renkey. Thermal conductivity of refractory castables. *J. Amer. Cer. Soc.* **1963** *46*(2), 89-92.

47. Hansen, W. C., and A. F. Livovich. Thermal conductivity of refractory insulating concrete. *J. Amer. Cer. Soc.* **1953** *36*(11), 356-362.

48. Kingery, W. D., and M. C. McQuarrie. Thermal conductivity: I. Concepts of measurement and factors affecting thermal conductivity of ceramic materials. *J. Amer. Cer. Soc.* **1954** *37*(2), 67-72.

49. Crowley, Michael S., and Jack S. Young. Thermal conductivity of monolithic refractories. *Amer. Cer. Soc. Bull.* **1988** *67*(7), 1196-1200.

50. Norton, 1968, 304.

51. Barrett, L. R. Heat transfer in refractory insulating materials. *Trans. Brit. Cer. Soc.* **1949** *48*, 235-262.

52. Committee C-8 on Refractories. *Standard Classification of Alumina and Alumina-Silicate Castable Refractories*, ASTM C 401. Philadelphia: American Society for Testing and Materials, 1991.

53. Bates, Robert L. *The Geology of the Industrial Rocks and Minerals* (New York: Dover Publications, 1969), 50-57.

54. Anonymous. *Basic Facts About Perlite*. Staten Island, NY: Perlite Institute, n.d.

55. Harben, Peter W. *The Industrial Minerals Handybook*, 2d ed. (London: Metal Bulletin, 1995), 126-128.

56. Neisel, R. H., and J. D. Verschoor. Thermal insulation. Mark, Herman F., Donald F. Othmer, Charles G. Overberger, and Glenn T. Seaborg, Eds. *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 13 (New York: Wiley, 1981), 591-605.

57. Fowler, 55.

58. Griffiths, Joyce, Ed. *Industrial Minerals Directory*, 2d ed. (London: Metal Bulletin, 1991), 524-525.

59. Grimshaw, Rex W. *The Chemistry and Physics of Clays and Allied Ceramic Materials*, 4th ed. (New York: Wiley, 1971), 154-155.

60. Klein, Cornelius, and Cornelius S. Hurlbut Jr. *Manual of Mineralogy*, 21st ed. (New York: Wiley, 1993), 666.

61. Gruner, John W. Ammonium mica synthesize from vermiculite. *Amer. Mineral.* **1939** *24*, 428-433.

62. Klein and Hurlbut, 505-518.

63. Krauskopf, Konrad B., and Dennis K. Bird. *Introduction to Geochemistry*, 3d ed. (New York: McGraw-Hill, 1995), 343.

64. Mason, Brian, and L. G. Berry. *Elements of Mineralogy* (San Francisco: W. H. Freeman, 1968), 447-448.

65. Myers, John B. Vermiculite. In Gillson, Joseph L., Ed. *Industrial Minerals and Rocks* (New York: American Institute of Mining, Metallurgical, and Petroleum Engineers, 1960), 889.

66. Hancock, 35-36.

67. Shaw, 43.

68. Shaw, 72-89.

69. Hancock, 115.

70. Neville, Adam, and P. J. Wainwright. *High Alumina Cement Concrete* (New York: Wiley, 1975), 1-15.

71. Robson, T. D. Aluminous cements and refractory castables. Taylor, H. F. W., Ed. *The Chemistry of Cements* (London: Academic Press, 1964), 3-35.

72. George, C. M. Industrial aluminous cements. Barnes, P., Ed. *Structure and Performance of Cements* (London: Applied Science Publishers, 1983), 415-470.

73. MacZura, George, LeRoy D. Hart, Raymond P. Heilich, and Joseph E. Kopanda. Refractory cements. *Cer. Sci. Eng. Proc.* **1983** *4*(1-2), 46-67.

74. Kopanda, J. E., and G. MacZura. Production processes, properties, and applications for calcium aluminate cements. Hart, L. D. Ed. *Alumina Chemicals: Science and Technology Handbook* (Westerville, OH: American Ceramic Society, 1990), 171-183.

75. Funk, James F., and Dennis R. Dinger. Particle size control for high-solids castable refractories. *Amer. Cer. Soc. Bull.* **1994** *73*(10), 66-67.

76. Gitzen, W. H., L. D. Hart, and G. MacZura. Properties of some calcium aluminate cement compositions. *J. Amer. Cer. Soc.* **1957** *40*(5), 158-167.

77. Tseung, A. C. C., and T. G. Carruthers. Refractory concretes based on pure calcium aluminate cement. *Trans. Brit. Cer. Soc.* **1963** *62*, 305-320.

78. Popovics, Sandor. *Concrete Materials: Properties, Specifications and Testing*, 2d ed. (Park Ridge, NJ: Noyes Publications, 1992), 160-165.

79. Sutton and Thrower, DM-15.

80. Fabianic, W. L. Microscopic control of particle size in refractory manufacture. *J. Amer. Cer. Soc.* **1935** *18*(1), 23-25.

81. Whittemore, O. J. Jr. Particle compaction. Onoda, George Y. Jr., and Larry L. Hench, Eds. *Ceramic Processing Before Firing* (New York: Wiley, 1978), 343-356.

82. MacZura, George, V. Gnauck, and Paul T. Rothenbuehler. Fine aluminas for high performance refractories. Paper presented at the First International Conference on Refractories, Tokyo, Japan, November 15-18, 1983.

83. Burroughs, Robert W., and Leonard P. Krietz. Relationship and quality control in the refractory manufacturing system. *Amer. Cer. Soc. Bull.* **1991** *70*(7), 1180-1182.

84. Anonymous. *Plasmal™ Lightweight Alumina Aggregate*, Product Data Sheet F35-15717. Pittsburgh: Alcoa Industrial Chemicals, December 19, 1995.

85. MacZura, George, Personal communication, November 4, 1995.

86. Committee C-8 on Refractories. *Standard Test Method for Pyrometric Cone Equivalent (PCE) of Fireclay and High Alumina Refractory Materials*, ASTM C24. Philadelphia: American Society for Testing and Materials, 1989.

87. MacZura, G., and K. J. Moody. New high temperature insulating aggregates. Paper presented at the American Ceramic Society, Refractory Ceramic Division Meeting, Huron, Ohio, October 6-7, 1995.

88. MacZura, George. Alumina: calcined, tabular, and alumina cements. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed. Vol. 2. (New York: Wiley, 1989), 302-317.

110

89. Misra, Chanakya. *Industrial Alumina Chemicals* (Washington, DC: American Chemical Society, 1986), 3-20.

90. Hughes, Richard W. *Corundum* (London: Butterworth-Heinemann, 1990), 1-33.

91. Moody, Ken. New high-alumina insulating aggregates. *Ceramic Industry* **1996** *145*(2), 42-45.

92. Stevens, R., and J. G. P. Binner. Structure, properties and production of β-alumina. *J. Mater. Sci.* **1984** *19*, 695-715.

93. Committee C-8 on Refractories. *Standard Test Methods for Apparent Porosity, Water Absorption, Apparent Specific Gravity, and Bulk Density of Burned Refractory Brick and Shapes by Boiling Water*, ASTM C20. Philadelphia: American Society for Testing and Materials, 1992.

94. Moody, Ken. Personal communication, October 20, 1995.

95. Ulrich, Karl T., and Steven D. Eppinger. *Product Design and Development* (New York: McGraw-Hill, 1995), 14-32.

96. Wheelwright, Steven C., and Kim B. Clark. *Revolutionizing Product Development: Quantum Leaps in Speed, Efficiency, and Quality*. (New York: Free Press, 1992), 218-244.

97. Box, George E. P., William G. Hunter, and J. Stuart Hunter. *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building* (New York: Wiley, 1978), 21-105.

98. Krause, 116-232.

99. Technical Committee on Industrial Classification. *Standard Industrial Classification Manual*. Washington, DC: Executive Office of the President, Office of Management and Budget, 1987.

100. U.S. Department of Commerce. *1992 Census of Manufacturers: Cement and Structural Clay Products*, MC92-I-32B. Washington, DC: U.S. Government Printing Office, 1992.

101. U.S. Department of Commerce. *1992 Census of Manufacturers: Abrasive, Asbestos, and Miscellaneous Nonmetallic Mineral Products*, MC92-I-32E. Washington, DC: U.S. Government Printing Office, 1992.

102. Miller, Robert F. Personal communication, March 14, 1996.

103. Gensch, Dennis H., Nicola Aversa, and Steven P. Moore. A choice-modeling market information system that enabled ABB Electric to expand its market share. *Interfaces* **1990** *20*, 6-25.

104. Urban, Glen L., and John R. Hauser. *Design and Marketing of New Products*, 2d ed. (Englewood Cliffs, NJ: Prentice-Hall. 1993), 110-114.

105. MacZura, George, and Kenneth Moody. Personal communication, October 1995.

106. Committee C-8 on Refractories. *Standard Practices for Determining and Measuring Consistency of Refractory Concretes*, ASTM C 860. Philadelphia: American Society for Testing and Materials, 1991.

107. Committee C-1 on Cement. *Standard Test Methods for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)*, ASTM C 109. Philadelphia: American Society for Testing and Materials, 1995.

108. Anonymous. *Harborlite Technical Data Sheet: UC-216*. Vicksburg, MS: Harborlite, n.d.

109. Anonymous. *Harborlite Technical Data Sheet: IN-8*. Vicksburg, MS: Harborlite, n.d.

110. Anonymous. *Zonolite® Industrial Vermiculite*. Cambridge, MA: W. R. Grace, 1989.

111. Anonymous. *Duralum AB Bubbles*. Niagara Falls, NY: Washington Mills Electro Minerals, n.d.

112. Anonymous. *CA-14 Calcium Aluminate Cement*, CHE 950A. Bauxite, AR: Alcoa Industrial Chemicals, April 1994.

113. Anonymous. *CA-25 Calcium Aluminate Cement, Regular Grade*, CHE 950. Bauxite, AR: Alcoa Industrial Chemicals, April 1994.

114. Givan, Guy V., LeRoy D. Hart, Raymond P. Heilich, and George MacZura. Curing and firing high purity calcium aluminate-bonded tabular alumina castables. *Amer. Cer. Soc. Bull.* **1975** *54*(8), 710-713.

115. Holterfoff, Adam. Personal communication, October 16, 1995.

116. Anonymous. *Calcium Aluminate Cements and Mortars*. Allentown, PA: Lehigh Portland Cement, December 1995.

117. Anonymous. *SAPPHIRE*. Mayfield, KY: Kentucky-Tennessee Clay, n.d.

118. Anonymous. *Typical Properties Reference: Ball Clay, Kaolin, Feldspar.* Mayfield, KY, April 1995.

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9.0 Appendix

Refractory suppliers in the U.S. market are given in Table A-1. Sources used to identify these companies are given on page 51.

Table A-1. Refractories Suppliers in the U.S. Market

Company	Location
Advanced Cerametrics	Lambertville, NJ
Aerospace Coating System	Berlin, CT
Aerospex	National City, CA
Allied Mineral Products	Columbus, OH
Alltherm Services	Highland, IN
Alsey Refractories	St. Louis, MO
Amtec Industries	Cleveland, OH
Applied Ceramics	Atlanta, GA
Aremco Products	Ossining, NY
Atlas Foundry	Tacoma, WA
B & B Refractories	Santa Fe Springs, CA
Baker Refractories	York, PA
Bartley Crucible & Refractories	Trenton, NJ
Benchmark Structural Ceramics	Buffalo, NY
Bigelow-Liptak	Watertown, NY
Black Products	Chicago, IL
Blasch Precision Ceramics	Albany, NY
BMI Colorado Refractories	Canon City, CO
BMI Refractories	Carnegie, PA
BNZ Materials	Littleton, CO
Bolt Technical Ceramics	Conroe, TX
Carborundum, Fibers Division	Niagra Falls, NY
Carborundum, Monofrax Refractories	Falconer, NY
Carborundum, Performance Refractories	Keasbey, NJ
Ceradyne	Costa Mesa, CA
Ceradyne Thermo Materials	Scottdale, GA
Ceramic Fiber Fabrication	Yucca Valley, CA

Table A-1. Refractories Suppliers in the U.S. Market

Company	Location
Ceramic Fillers	Atlanta, GA
Chi-Vit	Urbana, OH
Chicago Fire Brick	Chicago, IL
Christy Refractories	St. Louis, MO
Consolidated Ceramic Products	Blanchester, OH
Coors Ceramics	Golden, CO
Coors Wear Products	Lawrence, PA
Coppers Refractory Materials	Carrollton, OH
Corhart Refractories	Louisville, KY
Corson Refractories	Lebanon, PA
Corundite Refractories	Massillon, OH
Crescent Brick	East Canton, OH
Custom Casting, Inc.	Mokena, IL
Custom Electric Manufacturing	Wixom, MI
Delkic & Associates/International Technical Ceramics	Ponte Vedra Beach, FL
E. R. Advanced Ceramics	East Palestine, OH
Emhart Refractories/LaClede Christy Caly Products	Owensville, MO
Engineered Ceramics	Gilberts, IL
Eternit	Blandon, PA
Fels Refractories	Edison, NJ
Ferro, Special Ceramics Division, Cesco Plant	Crooksville, OH
Ferro, Special Ceramics Division, Louthan Plant	East Liverpool, OH
Fibrex	Aurora, IL
Findlay Refractories	Washington, PA
Fireline	Youngstown, OH
Fosbel	Berea, OH
Foseco	Cleveland, OH

Table A-1. Refractories Suppliers in the U.S. Market

Company	Location
Freeport Area Enterprises	Freeport, PA
A. P. Green Industries	Mexico, MO
Harbison-Walker Refractories	Pittsburgh, PA
Heatshield Technologies	Pompano Beach, FL
Hi-Tech Ceramics	Alfred, NY
Industrial Ceramic Products	Columbus, OH
Industrial Insulations	City of Industry, CA
Industrial Products International	Englewood, CO
Inland Refractories	Avon, OH
Insul	East Palestine, OH
International Technical Ceramics	Ponte Vedra Beach, FL
Ipsen Ceramics	Pecatonica, IL
J. H. France Refractories	Snow Shoe, PA
Kittanning Brick	Adrian, PA
Lee Goebel Specialty Products	Brea, CA
Lindberg	Watertown, WI
Louisville Fire Brick Works	Louisville, KY
Lynn Products	Lynn, MA
Magneco/Metrel	Addison, IL
Martin Marietta Magnesia Specialties	Baltimore, MD
Maryland Refractories	Irondale, OH
Matrix Refractories	Chicago, IL
McNeil Insulation	Newark, NJ
Metsch Refractories	Chester, WV
Minteq International	Easton, PA
Missouri Refractories	St. Louis, MO
Mitsubishi International	Pittsburgh, PA

Table A-1. Refractories Suppliers in the U.S. Market

Company	Location
Mt. Savage Refractories	Pittsburgh, PA
National Refractories & Minerals	Livermore, CA
New Castle Refractories	New Castle, PA
Nock & Son	Cleveland, OH
North American Refractories	Cleveland, OH
North State Pyrophyllite	Greensboro, NC
Norton Pakco Industrial Ceramics	Latrobe, PA
Novel Technologies	Cayuga, NY
Oglebay Norton, Refractories & Minerals Group	Cleveland, OH
Ozark Technical Ceramics	Webb City, MO
Pell Industries	Grove City, PA
Permatech	Graham, NC
Plibrico	Chicago, IL
Premier Refractories & Chemcials	King of Prussia, PA
Pryor-Giggey	Chehalis, WA
Pyro Engineering	Santa Fe Springs, CA
Refco	Pittsburgh, PA
Refractory Products	Elgin, IL
Refractory Sales & Service	Bessemer, AL
Refractory Technology	Gurnee, IL
Reno Refractories	Morris, AL
Resco Products	Norristown, PA
Riverside Refractories	Pell City, AL
Rocky Mountain Refractories	Salt Lake City, UT
Saint Gobain/Norton Industrial Ceramics	Worcester, MA
Salazar & Sons	River Forest, IL
Schlosser Casting	Redmond, OR

Table A-1. Refractories Suppliers in the U.S. Market

Company	Location
Selee	Hendersonville, NC
Servsteel	Morgan, PA
Shenango Refractories	New Castle, PA
Skamol	Niagra Falls, NY
Spar	Jacksonville, AL
Superior Technical Ceramics	St. Albans, VT
Thermal Ceramics	Augusta, GA
Thermal Products	Norcross, GA
Thermatex	Newton Falls, OH
Thermic Refractories	Girard, IL
TYK Refractories	Clairton, PA
Unicast Development Group	Pleasantville, NY
United Refractories	Warren, OH
United States Refractories	Jacksonville, FL
Universal Specialties	Pittsburgh, PA
Vanalco	---
Vesuvius	Naperville, IL
Vesuvius-McDanel	Beaver Falls, PA
Vgt-Dyko Industrial Ceramics	Louisville, KY
Wahl Refractories	Fremont, OH
Wellsville Fire Brick	Wellsville, OH
Wesco Refractories	Fort Worth, TX
Whip-Mix	Louisville, KY
Whitacre-Greer Fireproofing	Waynesburg, OH
Wulfrath Refractories	Tarentum, PA
Zedmark, Division of Minteq International	Dover, OH
Zedmark, Division of Quigley	Slippery Rock, PA

Table A-1. Refractories Suppliers in the U.S. Market

Company	Location
Zircar Products	Florida, NY
Zircoa	Solon, OH