

STATE-OF-THE-ART REPORT

REFRACTORY PLASTICS AND RAMMING MIXES

Reported by ACI Committee 547

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This report addresses the range of current technology and application experience for refractory plastics and ramming mixes. A brief discussion of the past and present history of plastics and ramming mixes is presented to establish the usefulness and adaptability of these refractory compositions.

The design, installation, and repair of refractory plastic and ramming mix linings are discussed with criteria for proper selection. The general characteristics and standardized test procedures are designed to provide instruction and direction in the proper design and installation of the refractory lining.

Installation, construction, proper drying procedures, and repair methods are presented to provide a reference point when deciding the details of engineering design of a furnace or the quick repair of existing equipment.

Chapters 8 and 9 provide ample discussions on applications and the newest developments in the use and performance of plastics and ramming mixes in various types of industries with improved methods for installing these refractory compositions.

Key Words: abrasion; adhesion; aggregates; anchors (fasteners); binders (materials); bulk density; castable refractories; cement additives (clinker); cement additives (raw material); ceramics, bond; cohesion; compressive strength; construction joint; control joints; corrosion; creep properties; curing; drying; electrical resistance; erosion; firing; flexural strength; grog; gunning; hygroscopicity; laminates; linear properties; permeability; porosity; refractories; resiliency; shelf life; spalling; thermal conductivity; thermal expansion; thermal shock; thermal stress; vents; walls.

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CHAPTER 1 -- INTRODUCTION

1.1 -- Objective

This report describes the state-of-the-art in the use of plastics and ramming mixes for refractory applications. It complements a similar report of ACI Committee 547 entitled "Refractory Concrete" (ACI 547R-79). The latter describes the technology of refractory concretes, most of which use calcium aluminate cement as the binder.

This document provides a source of information on the technology of materials classified as plastic refractories and ramming mixes. It is neither a standard specification nor a classification and should not be used for those purposes.

ACI Committee 547 was organized in 1969 to provide a reliable and comprehensive source of information on monolithic refractories technology including refractory concrete, plastic refractories and ramming mixes. To accomplish this mission, the Committee has sponsored various seminar-workshops, symposia and publications. This report is another step in the development of an objective and definitive consensus based on experience and on the literature.

1.2 -- Scope

In many respects, plastics and ramming mixes are very similar. Accordingly, the term "plastics" will be used throughout this report to represent both plastic refractories and ramming mixes. When differences occur, these will be noted in the text.

Plastics (sometimes referred to as “moldables”) and ramming mixes are manufactured from similar ingredients. They differ primarily in moisture content and particle size gradation, the plastic refractories being more moldable because of a higher moisture content.

Some plastics are gunned in place and the moisture content of these can vary widely. For such materials, the distinction between plastics and ramming mixes is not precise.

Plastics usually consist of a clay and either alumina, magnesite, chrome ore, silicon carbide or graphite as an aggregate base. They are blended with specific binders such as clay or phosphoric acid for heat-setting and clay or sodium silicate for air-setting. Special properties, such as resistance to acid or slag attack, freezing and low temperature hardening, may be achieved by including appropriate additives. Plastics can be designed for use to maximum service temperatures of 3400 F (1870 C) and some of the commercial ramming mixes have a 4000 F (2200 C) service temperature limit.

Packaged plastics are available in either a moist “ready to use” form or dry. Water is usually added to the dry form at the job site.

Monolithic construction, repairs or the molding of special shapes are usually performed by ramming the materials into place with a mallet or pneumatic tool. Some dry types are suitable for gunning. A recently developed vibratable plastic combines the properties of a plastic and the ease of concrete installation.

This report covers the following phases of plastic refractories technology: Constituent ingredients, manufacturing processes, material characteristics, selection criteria, testing, installation techniques, drying and firing, construction details, repair procedures, current applications and anticipated future developments.

The Refractories Institute maintains an information service and publishes a directory which lists all United States refractory material manufacturers and the brand names of their products.

1.3 -- Glossary of terms*

abrasion--a wearing away of a solid surface by rubbing, scouring or friction action of moving solids.

acid refractories--refractories containing a substantial amount of silica that may react chemically with basic fluxes, basic slags, or basic refractories at high temperatures. Although technically not correct, alumina is generally considered an acid refractory.

aggregate--any coarse granular refractory material.

air-setting refractories--compositions of finely ground refractory materials which harden upon drying in air.

anchor--a metal or ceramic support for attaching the refractory to an adjacent structure.

basic refractories--refractories whose major constituent is lime, magnesia, or both, and which may react chemically acid fluxes, acid slags, or acid refractories at high temperatures. (Commercial use of this term also includes refractories made of chrome ore or combinations of chrome ore and dead burned magnesite.)

* See ASTM C 71 for additional information on definitions.

binder--“cementing” material.

bloating--substantial swelling produced by heat that causes the formation of a vesicular structure.

calcium aluminate cement--the product, which consists of hydraulic calcium, obtained by pulverizing clinker aluminates formed by fusing or sintering a suitably proportioned mixture of aluminous and calcareous materials.

castable refractory--a dry mixture of a binder, usually calcium aluminate cement, and selected and proportioned refractory aggregate(s) which when mixed with water produces a solid.

casting--the process of placing wet mixed refractory concrete by rodding or vibration.

ceramic bond--the high strength bond developed between materials as a result of thermo-chemical reactions which occur at elevated temperature.

chemical setting--developing a strong bond by chemical reaction.

cold face--the surface of a refractory section not exposed to the source of heat. Commonly the surface furthest from the source of heat.

cold setting refractories--a composition which develops a bond at normal ambient temperature prior to drying.

construction joint--see joint.

comminution--reduction of materials to fine particles.

compactability--the ease with which the volume of a freshly placed plastic refractory or ramming mix is reduced to a practical minimum, usually by ramming.

corrosion--disintegration or deterioration or chemical attack including electrolysis.

creep--time-dependent deformation due to sustained load.

curing--maintenance of humidity and temperature of freshly placed concrete during some definite period following placing, casting or finishing to assure satisfactory hydration of the cementitious materials (when present) and proper hardening of the concrete.

drying--removal of free moisture from a material.

erosion--progressive disintegration of a solid by the abrasion or cavitation action of gases, liquids or solids in motion.

expansion joint--a separation between adjoining parts of a refractory lining to allow small expansive movements, such as those caused by thermal changes.

explosive spalling--a sudden fragmentation of the castable which occurs as the result of a buildup of steam pressure due to inappropriately rapid heating generally on first firing.

extrude--to force a plastic refractory through a die by the application of pressure.

field mix--a mix formulated at or near the job site.

firing--the process of heating refractories to develop desired properties.

grog--see aggregate.

gun-casting--a method of placing castables using a pneumatic gun as a conveyor of the material by reducing the velocity of the castable at the nozzle.

gunning--act of applying refractory, which is emplaced by projecting onto a surface via an air placement gun.

gunning mix--a refractory mix which is emplaced by projecting onto a surface via an air placement gun.

heat-setting--requiring heat to promote bonding.

hydraulic cement--a cement that sets and hardens by chemical interaction with water and that is capable of doing so under water.

insulating castable--a castable with relatively low thermal conductivity; it usually has a low in-place density (less than 100 lb/ft³, 1.6 Mg/m³).

joint (also construction joint)--a separation between adjacent parts of a refractory construction.

lamination--plane of weakness which permits separation into layers.

lightweight castable--see insulating castable.

matrix--the continuous phase in the emplaced refractory.

monolithic refractory--refractories in which joints are minimized after installation.

neutral refractories--refractories that are equally resistant to chemical attack by both acid and basic slags or fluxes at high temperatures.

normal weight refractory concrete--refractory concrete having a unit weight greater than 100 lb/ft³ (1.5 Mg/m³) in place.

plastic refractories--refractory materials possessing adequate plasticity to be shaped in the field.

plasticity--a property of a material which allows it to be molded or shaped.

punkiness--friable spongy appearance.

ramming mix--a granular refractory material which has suitable properties to permit ramming into place to form a monolithic structure.

rebound--material which bounces off the surface against which it is being gunned.

setting--the hardening that occurs with time and/or temperature.

sheeting--spalling of layers from the hot face of the refractory.

shelf life--maximum interval during which a material may be stored and remain in a usable condition.

steam spalling--see explosive spalling

thermal shock--exposure of a material to one or more rapid changes in temperature which may have a deleterious effect on the integrity of the refractory.

thermal spalling--fragmentation of a solid as the result of stresses caused by thermal shock.

thixotropic--a material which flows more easily under shear forces flows.

vent--an opening into the hot face of the monolithic refractory to permit escape of gas or steam during drying and firing.

wall seat--a support for a vertical element of refractory.

weephole--an opening at the cold face to permit the escape of moisture.

1.4 -- History

The origins of refractories usage can be traced to the ancient art of making brick by using commonly occurring clays. Modern plastic refractories technology began when a proprietary refractory "plastic firebrick" (a calcined aggregate bonded with fireclay) was introduced in 1914. When mixed with water, it provided a suitable patching material for refractory linings in boilers. This material was used sparingly for the next ten years.

Considerable commercial development of the monoliths occurred during the "decade of the twenties." The terms "plastic firebrick," "plastic refractories," "refractory mortar" and

“refractory concrete” were used interchangeably. This new material was a mixture of crushed firebrick and high temperature cement blended with a minimum quantity of water, or waterglass, or both. It was rammed into place within wooden forms, which were usually removed by burning during the heating process.

By the late 1930s, experience gained from the increased use of plastic refractories resulted in a better understanding of the material capabilities. This, in turn, led to improved installation techniques and the development of additional products for a wider range of applications.

Plastics began to be considered as a viable alternative to the use of firebrick. Plastic refractories simplified construction of complex configurations which, previously, had required many special prefired shapes. The demand for refractories during World War II accelerated the use of plastics and this led to a dramatic rise in their production.

Compared to brick, plastics have the following advantages for refractory construction:

- Ease of manufacture,
- Lower energy requirements for manufacture,
- Short installation time,
- Minimum use of skilled labor,
- Excellent patching characteristics for repairs,
- With proper anchoring, plastics withstand bulging and expansion better than brick construction,
- Elimination of joints minimizes leakage, and
- Lower thermal conductivity.

Forecasters predict that the use of monoliths, and particularly plastics, will continue to expand. New developments in refractory technology are resulting in more sophisticated plastics with enhanced physical and chemical properties. These new products will provide engineers with improved materials for solving the complex refractory problems of the future.

1.5 -- Status in the United States

The Census Bureau (1) began using the term “plastic firebrick” in 1939. The recorded gross value of these materials, in comparison to all refractories, was 2.6 percent in 1937 and 2.8 percent in 1939. When the term “plastic refractories” (including wet and dry ramming mixes) was introduced by the Census Bureau in 1947, the percentage had risen to only 3.0 percent. From 1947 to 1978, clay and nonclay refractories reflected a seven-fold increase in total value, whereas plastics increased about fortyfold.

Statistics for nonclay plastics in 1947 appeared in the 1954 census report but not in the 1947 report. The high alumina plastics (50 to 87.5 percent Al_2O_3) were listed separately in 1974. Phosphate-bonded high alumina plastics (greater than 50 percent Al_2O_3) were first listed in 1982.

Since 1947, the production and use of plastics has more than tripled, and the trend continues upward. Shipments of both clay and nonclay plastics exceeded 490,000 tons in 1978 (2). This represents a net value of approximately \$145,000,000, or about 10 percent of the total value of all refractories shipped during 1978.

The iron and steel industry is the largest user of plastics. As shown in Table 1.5, significant amounts are also used in other industries.

Table 1.5 -- Use of plastics (1982 estimates) on the basis of shipped weights

<u>Industry</u>	<u>Percent</u>
Iron & Steel	49
Power Generation and Incineration	20
Nonferrous Metals	15
Hydrocarbons and Chemicals	8
Mineral Processing (cement, lime, etc.)	6
Ceramics	1
Glass	1

1.6 -- Comparison with other refractories

The design of a refractory installation is a complex, sometimes difficult and uncertain, procedure. Because one type of product rarely satisfies all conditions that can exist within a process vessel, a knowledge of the entire spectrum of refractories is usually required. Refractory concrete is discussed in ACI 547R. Other types of refractory are discussed briefly in Section 1.6 of the same report and include refractory brick, concrete, mortars and coatings and special gunning mixes. Ceramic fibers and block-type insulation are also used as refractories.

For new construction, the choice between plastics and other types of refractories usually depends on economics and the design requirements. For repair work, however, other considerations, such as minimizing downtime, are important considerations in the choice of material (see [Chapter 7](#)). Each material has distinct qualities and advantages that influence selection for a specific application.

1.6.1 Plastics versus castables -- The service capabilities of plastics and castables differ because of their physical and chemical makeup. Each can be used for a specific purpose, either side by side or in separate locations of a heat-containment vessel. In many applications, both are replacing firebrick. This trend is expected to continue with further improvements in aggregate and binder technology.

Plastics are formulated to be used in the same temperature regimes as castables. Except for the phosphate-bonded plastics cured above 600 F (315 C), the hot and cold strengths

of plastics are generally lower than those of concretes. The strength variation through the cross-section of the lining (lower on the cool face) is greater with plastics. The strength reduction of refractory concretes in the intermediate temperature range is not observed in plastics. Most plastics are more resistant to spalling and to chemical and slag attack than are concretes.

Plastics can generally be placed without the use of forms. In contrast, refractory concretes require forms except when applied by gun or trowel. Placement of refractory concrete can normally be accomplished faster than for plastics. However, the mixing, forming, curing, drying and firing schedules are usually more complex than with plastics.

The final selection of either a plastic or castable will be determined by its ability to meet the design criteria and its cost-effectiveness. It is recommended that the refractories manufacturer be consulted prior to specification and use of a particular material.

CHAPTER 2 -- CONSTITUENT INGREDIENTS AND MANUFACTURING METHODS

2.1 -- Introduction

Ingredients used in the manufacture of ramming mixes, plastics and patching mixes include aggregate, matrix and binders. The final product is a function of aggregate type and gradation, matrix content and binder type and content. However, not all aggregate, matrix and binder combinations are usable. Inappropriate combinations can lead to such undesirable phenomena as premature hardening during storage, poor installation characteristics, spalling during heat-up and loss of strength and integrity due to liquid phase development or volume change during service.

2.2 -- Particle size/moisture level

Particle size is one of the major differences between the aggregate and the matrix. In general, aggregate materials range in size from about 1 mm to 9 mm, although milled aggregate smaller than 0.5 mm is sometimes used. Matrix and binder ingredients are usually 0.5 mm and smaller, with some clay particles as small as $0.01\mu\text{m}$. By segregating aggregates into different particle size fractions, they can be used at different concentrations and in combination with varying amounts of matrix and binder ingredients to produce ramming mixes, plastics and patching mixes. Typical product particle size distributions are shown in [Fig. 2.2](#) and, together with moisture levels, are discussed in the following paragraphs.

2.2.1 Ramming mixes and plastics -- Similar aggregate sizes are used in plastics and ramming mixes with the largest aggregate usually about 5 mm, though sometimes increasing to about 9 mm. The major difference between plastics and ramming mixes is the moisture level and workability. The moisture level for ramming mixes is typically 0 to 8 percent, while plastics have 5 to 18 percent. The workability (ASTM C 181) of ramming mixes is 15 percent or less, whereas plastics usually fall in the range of 15 to 40 percent.

2.2.2 Patching mixes -- Patching mixes (sometimes called patching plasters) employ aggregates significantly smaller than those used in plastics. The moisture levels range from 8 to 15 percent.

2.3 -- Aggregates

Aggregates make up 50 to 80 percent by weight of plastics. As a result, they are the greatest contributor to the overall chemical composition of the product and their chemistry

TYLER SCREEN ANALYSIS

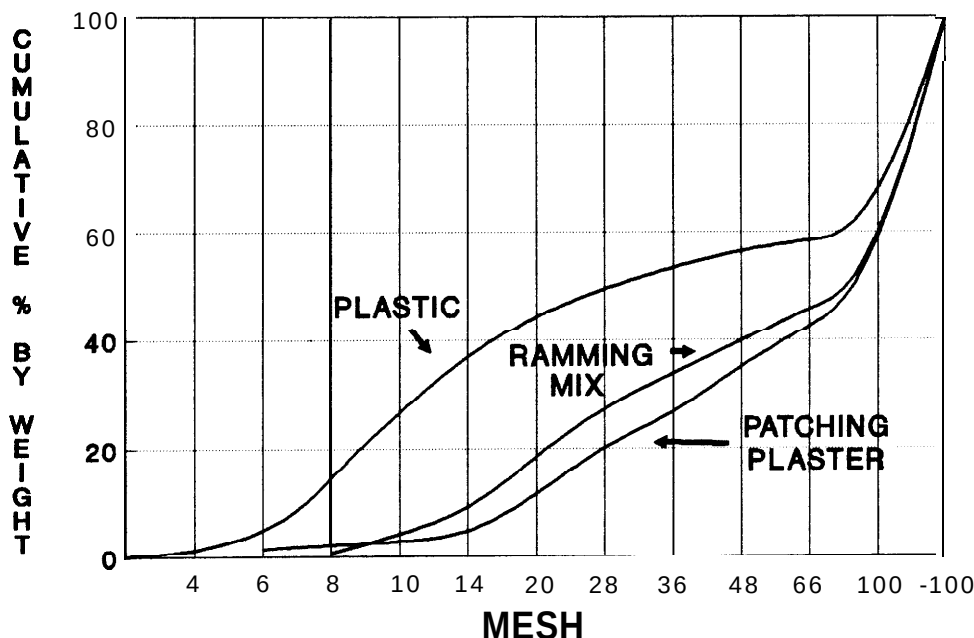


Fig. 2.2--Typical screen analysis of plastics and ramming mixes

dictates the type and/or amounts of matrix and binder ingredients. In general, aggregates are divided into two classes, acid-neutral and neutral-basic, based on their chemical composition.

2.3.1 Acid-neutral aggregates -- The majority of types (though not of tonnage) of plastics and patching mixes utilize acid-neutral aggregates. A significant portion of these aggregates can be found in the alumina-silica system and can range in chemistry from near 100 percent Al_2O_3 to 100 percent SiO_2 . Other aggregates, such as zirconia and silicon carbide, are also used. A list of these aggregate types, their alumina content, and their potential maximum service temperatures are shown in [Table 2.3.1](#).

2.3.2 Neutral-basic aggregates -- A number of the large tonnage ramming mixes, and a few plastics, are manufactured with neutral-basic aggregates. These aggregates include chrome ore, sintered magnesia, dolomite and olivine. Because of the tendency of the aggregate to hydrate, the majority of these products are furnished dry. The exceptions are chrome ore and olivine based formulations. Other than those produced from milled aggregate, most products use low levels of matrix ingredients.

2.4 -- Fine grained additives

Fine grained materials are added to control handling and installation characteristics such as compactability, plasticity, cohesion and adhesion. In addition, these ingredients provide the means to control the chemical composition. They can also reduce the effects

Table 2.3.1 -- Acid-neutral aggregates

<u>Designation</u>	Al_2O_3 percent	<u>Potential Maximum Service Temperature</u>	
		deg F	deg C
White Fused Alumina	100	3400	1870
Tabular Alumina	99.5	3400	1870
Brown Fused Alumina	97	3200	1760
Calcined Imported Bauxite	75-90	3200	1760
Mullite	59-60	3200	1760
Calcined Domestic Bauxite	88	3100	1705
Andalusite	60	3200	1760
Sillimanite	60	3200	1760
Calcined Kaolin	44-48	3000	1650
Crushed Firebrick	35-70	3000	1650
Calcined Clay Up to	40	2900	1595
Pyrophyllite	20-25	2500	1370
Quartz	0	2800	1540
Silicon Carbide	0	3000*	1650
Zirconia	0	3600	1980

* Atmospheric reducing conditions required, service limit much lower in oxidizing conditions.

of corrosive molten slags and metals, compensate for high temperature shrinkage, aid sintering and increase hot strength.

2.4.1 Comminuted aggregate -- A significant volume of fines is produced during milling of the aggregates. If additional fine grained material is required, it is obtained by pulverizing aggregate in devices such as ball mills and rod mills. Neutral-basic products use large quantities of milled aggregate. This is necessary to maintain the desired chemical composition, while providing a means to maximize particle packing. Milled aggregate generally consists of particles 0.1 mm and smaller. Ball milled aggregate usually consists of at least 50 percent particles smaller than 44 μm .

2.4.2 Calcines -- In addition to the milled aggregates mentioned in [Section 2.4.1](#), a significant number of the high alumina type plastics and patching mixes utilize relatively large quantities of calcined alumina and/or calcined clays. Calcined alumina helps optimize desirable oxide levels while reducing the overall impurity level. This provides good refractory characteristics and volume stability at elevated temperatures. Calcined alumina is generally used as particles 0.07 mm and smaller. Calcined clays assist in developing and maintaining plasticity while functioning as a primary sintering ingredient at elevated

temperatures. Calcined clays are generally used as particles 400m and smaller.

2.4.3 Shrinkage compensators -- Because of liquid development and sintering, some formulations are prone to excessive shrinkage at elevated temperatures. To compensate for such shrinkage, raw minerals such as, pyrophyllite, kyanite, sillimanite and quartz are used in limited quantities. Generally, these raw minerals are used in particle sizes 0.4 mm and smaller.

2.4.4 Graphite/carbon -- Some plastics are exposed to extremely corrosive molten slags under reducing conditions. These two deleterious conditions can often be counteracted by using graphite/carbon. The type, particle size and amount of graphite/carbon used is dependent on many variables including area of application, temperature, slag chemistry, hot strength requirements and binder type.

2.4.5 Additives -- A number of other matrix ingredients are used to perform specific functions. Chromia (Cr_2O_3) is added to increase slag resistance in oxidizing environments, enhance iron oxide penetration resistance and increase refractoriness. Silicon carbide is added to increase slag resistance in reducing environments, while enhancing hot strength. Examples of other special purpose additives are those used to protect graphite/carbon from oxidation and to reduce aluminum penetration. Many additives are considered proprietary or are protected by patents and/or licensing agreements.

2.5 -- Binder ingredients

Binder ingredients serve to impart cohesion during and after installation. The binder systems used in plastics and patching mixes range from simple raw clay and water to sophisticated resin/cross linking agent combinations. Dry and liquid binder ingredients can be used alone, or as a binder system in combination with sequestrants, anti-freeze agents and modifiers. Some of the binders currently in use are listed in [Tables 2.5.2 and 2.5.3](#).

Table 2.5.2 -- Liquid binder ingredients for plastics

Aqueous

Alginates
Aluminum Sulphate
Chromic Acid
Colloidal Silica Solution
Lignosulfonate
Resins
Mono-Aluminum Phosphate
Molasses
Phosphoric Acid
Potassium Silicate
Sodium Aluminum Phosphates
Sodium Silicate
Water

Nonaqueous

Coal Tars
Oils
Petroleum Tars

Binder systems can enhance plasticity, compactability, cohesion, adhesion capability in the green product and assist in sintering or high temperature bonding of the fired product.

2.5.1 Raw clays --Clays are important, not only as part of the bonding process, but also to impart plasticity in the green state. A wide variety of raw clays are available for the of the dry binders currently in use.

manufacture of plastics and patching mixes. These include ball clays, plastic clays, semi-plastic clays and bentonite. Air-floated kaolinite-type clays generally have particles between 20 and 0.2 μm . Bentonite has particles as small as 0.01 μm .

The type and amount of raw clay used in a product will depend on the aggregate used, the physical properties desired and the binder ingredients employed. Normally, bentonite will provide better storage characteristics for plastics with phosphate binder ingredients.

2.5.2 Binders for wet systems --Liquid binders can be either aqueous or nonaqueous. In general, aqueous binders are used with acid-neutral aggregates, whereas, nonaqueous binders are used with both acid-neutral and neutral-basic aggregates. The one notable exception to this general rule is chrome ore, which can be used with aqueous binders such as sodium silicate and chromic acid. **Table 2.5.2** is a partial list of some of the liquid binders currently in use in the refractory industry.

2.5.3 Binders for dry mixes --In dry ramming mixes, dry binders are generally used as sintering aids or high temperature bonding ingredients. **Table 2.5.3** is a partial list of some

Table 2.5.3 -- Dry binder ingredients for plastics

Aluminum Phosphates
 Aluminum Sulphate
 Boric Acid
 Colloidal Alumina
 Colloidal Silica
 Goulac
 Hydrated Alumina
 Lignosulfonate
 Methyl Cellulose
 Petroleum Pitches
 Resins
 Silica Fume
 Sodium Aluminum Phosphates
 Sodium Polyphosphates
 Sodium Silicate
 Starches
 Synthetic Clays
 Waxes

2.5.4 Modifiers and additives -- Sometimes binders do not, in themselves, impart all of the desired characteristics to the plastic. Modifiers and additives are used to compensate

for deficiencies such as, poor storage, poor compactability, reduced adhesion, reduced cohesion and processing difficulties during manufacture. Sequestrants, plasticizers, waxes

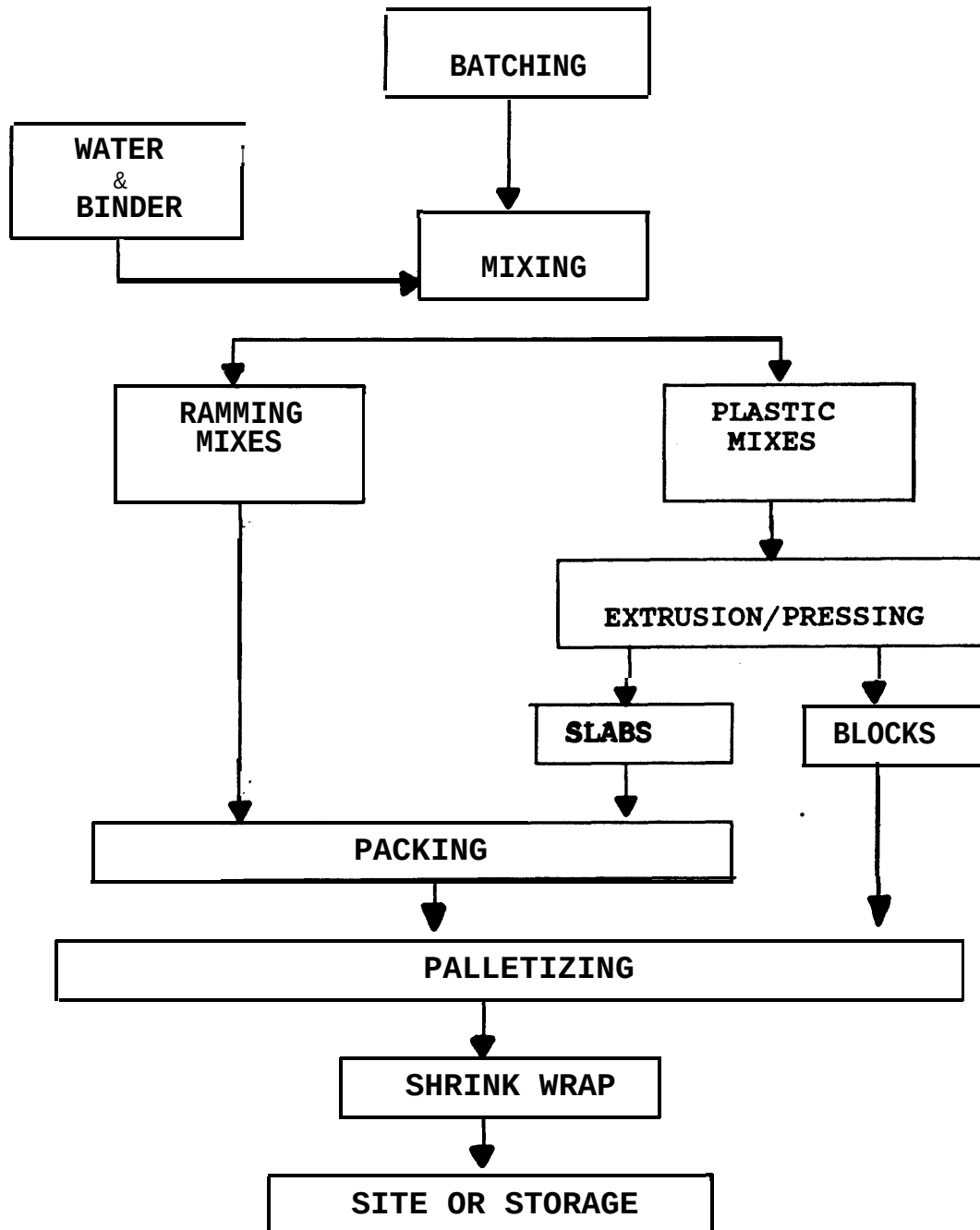


Fig. 2.6—Typical production flow sheet for manufacturers of plastic refractories

and extrusion aids are among the commonly used modifiers and additives.

2.5.5 Antifreeze agents-- During winter months, plastics which use aqueous binder systems may be subjected to freezing temperatures. If these products are used while their binder systems are partially frozen, their installation characteristics will be unacceptable. To overcome this limitation, antifreeze agents, such as methanol and ethylene glycol, are used to lower the freezing point to approximately 15 or 20 F (-9 or -7 C).

2.6 -- Manufacturing methods

Plastics are manufactured in batch quantities of one to two tons (900 to 1800 kg). Predetermined amounts of raw materials are weighed and introduced into a mixing device, usually some type of muller mixer. It is very important to mix and knead all of the raw material into a homogeneous mass, and to thoroughly distribute the water throughout the plastic.

The amount of water in plastics is usually controlled by a workability test (ASTM C 18). The workability of plasticity gradually decreases after manufacture.

Following mixing, the plastic is transferred into a ram or auger extruder, which compacts the material and extrudes a column of the correct cross section. Usually, the plastic is cut into slices as it emerges from the extruder and is wrapped in heavy paper to retard the escape of moisture. Normally, the plastic is placed in 100 lb (45 kg) cartons. Occasionally, however, it is placed directly in drums of 200 to 500 lb (90 to 230 kg) capacity.

Fig. 2.6 shows a typical production flow sheet for plastic refractories.

CHAPTER 3 -- CHARACTERISTICS AND TESTING

3.1 -- Introduction

Plastic refractories fall into three categories, plastics (including plastic block), ramming mixes and patching mixes. The bonding systems are generally ground raw clay and/or chemical bonds such as, sodium silicate (precipitation bonding), aluminum phosphate, phosphoric acid, aluminum sulfate and lignosulfonate. Generally, normal weight aggregates are used because lightweight (high porosity) insulating aggregates break down and densify during installation.

Measurement of the properties and characteristics of plastics is achieved through standardized test procedures. These measurements are especially important in the evaluation of materials for product development, performance assessment and quality control. The producer and user are cooperatively and independently involved in material testing.

3.2 -- Selection of a plastic refractory

The composition of plastics varies considerably and new mixes are being constantly developed. To provide a refractory suitable for a specific application, the user must inform the producer of the service conditions such as temperature, thermal cycling, erosion and corrosive environment. Candidate refractories must be evaluated in terms of refractoriness, thermal shock resistance, strength, etc., to determine their suitability for a specific

application. After establishing a suitable product, the producer must insure that the material quality is maintained throughout the processing of subsequent lots. Similarly, the user should satisfy himself that he is receiving the proper product and that quality is not changing.

3.2.1 Workability -- Workability index is the primary criterion used to differentiate plastic refractories and ramming mixes. Plastic refractories exhibit workability indices above 15 percent, while ramming mixes, which are pounded or rammed into place, generally have workability indices less than 15 percent. The workability index is determined by measuring the plastic deformation of a molded test specimen when subjected to impact (ASTM C 181).

3.2.2 Installation and start-up-- Proper installation of plastics is critical to obtaining the optimum properties and service life. The installer, who in many cases is an independent contractor, needs appropriate and reliable test information to properly place the refractory. Successful installation of a plastic requires reproducible testing by many parties and an exchange of procedures and results between the producer, user and installation contractor.

Once placed, the bond system determines the strength development of plastics. The three types of bond systems are termed air-setting, heat-setting and chemical.

Air-setting plastics harden to form a bond when exposed to drying conditions that permanently eliminate the free water. They will not harden under humid, still-air ambient conditions. Once hardened, they will soften if exposed to moist ambient conditions. Heat-setting plastics remain relatively weak until heated to temperatures sufficient to form a ceramic bond. Chemical bonds occur by chemical reactions at specific temperatures. Appropriate drying and firing procedures (See [Chapter 6](#)) are important in eliminating skin effects.

3.2.3 Test methods -- There are a number of standard test procedures for plastic refractories. At the present time, however, there are no international standards even though much study and effort has been expended toward this end. At the present time (1984), most test methods have been developed by BSI (British Standards Institute), DIN (Deutsche Industrie Normen) and ASTM (American Society for Testing and Materials). Most test methods in the U.S.A. follow ASTM specifications (3) and these are referenced in this report. The technology of plastics is still evolving and many tests, especially those used to characterize the materials before application, vary widely from product to product and producer to producer. Many of the presently used tests were developed for other types of refractories and have only limited applicability to plastics. When used for plastics, the results are affected by factors such as specimen handling, preparation, size, selection and moisture content. For some cases, ASTM standards require pressed specimens which may not be representative of the actual full scale plastic refractory installation.

3.3 -- Classification

3.3.1 Plastic refractories -- A plastic refractory consists of a mixture of refractory materials with sufficient clay and 5 to 18 percent water to give it a workable and cohesive texture for installation without further preparation. Often, the clay is the only binder and in many products, serves the primary purpose of transforming the product into a stiff, putty-like mass which will knit during installation. Installation is usually performed with

pneumatic rammers, generally without forms. The green material may range in consistency from very soft and unable to support its own weight, to extremely stiff.

Plastic refractories are normally produced by extrusion and are sliced into convenient segments for installation. Plastic blocks are extruded under a vacuum. This removes most of the air from the mix and creates a product approaching maximum density that requires no further forming. The blocks are generally laid up in position and tightly sealed. Joints are sometimes mortared to ensure better knitting. A few plastic refractories are made so they can be installed by vibration.

3.3.2 Ramming mixes -- Ramming mixes are manufactured from refractory materials which are graded to obtain a specific particle size distribution. Additives are often used to make the mixes workable and self-bonding. Ramming mixes are either premixed with 1 to 8 percent liquid, or packaged dry. Some of the dry ramming mixes are mixed with a liquid in the field, while others require no liquid addition before placement. Generally, ramming products are granular in form and are packaged in bags, drums or cartons.

Pneumatic rammers are used to install the wet mixes, resulting in a dense, low porosity mass. Dry mixes are consolidated with vibrators or pneumatic rammers into a dense packing arrangement. Ramming mixes are more difficult to install than plastics and are usually used in applications where maximum density, low shrinkage and low moisture are desired. During installation, forms are normally required to constrain the granular ramming mixes.

3.3.3 Patching mixes -- Patching mixes are generally soft, pliable products used for patching and repair, or for thin linings or coatings. Installation techniques vary with each situation. Because it is easy to contour these mixes to any shape, they are particularly suitable for quick and economical emergency repairs.

3.3.4 Classification systems -- **Table 3.3.4** is taken from ASTM C 673.

Table 3.3.4 -- Classification of fireclay and high alumina plastic refractories and ramming mixes (ASTM C 673)

<u>Class</u>	<u>Pyrometric Cone Equivalent, Min</u>	<u>Alumina Content, Percent</u>
High Duty	31	NR
Super Duty	32 ^{1/2}	NR
60 percent Alumina	35	57.6 to 62.5
70 percent Alumina	36	67.6 to 72.5
80 percent Alumina	37	77.6 to 82.5
85 percent Alumina	NR	82.6 to 87.5
90 percent Alumina	NR	87.6 to 92.5
95 percent Alumina	NR	92.6 to 97.5
100 percent Alumina	NR	> 97.5

NR = Not required

As shown in the table, ASTM classifies plastics by alumina content and refractoriness. The latter is measured by the pyrometric cone equivalent (PCE) test (ASTM C 24).

In some cases, plastics are classified according to the principal aggregate, such as chromia, silicon carbide, zirconia or magnesia. To aid classification and specification, chemical analyses are normally listed in product data sheets.

3.4 -- Chemical analysis

The chemical composition of plastics depends on the constituent raw materials. Methods of chemical analysis are discussed in [Section 3.6.1](#). The chemical analysis is usually presented on a calcined basis and, as can be seen in [Table 3.4](#), is expressed as the oxide. The product chemical analysis is a guide to the resistance of the plastic to acid and basic slags, and is important for material selection (see [Chapter 4](#)). The occurrence of the oxide as different mineralogical phases will strongly affect performance. This must also be considered (see [Chapter 2](#)).

Chemical composition is a factor in determining a product's utility, especially where there are unusual conditions in the process environment. For example, silica may be undesirable in hydrogen atmospheres and iron oxide undesirable in a carbon monoxide rich environment. Some metal oxide impurities can be dissolved from the plastic by molten metals and contaminate the alloy being processed.

3.5 -- Sampling

Like other ceramic products, plastics are not always homogeneous. The most carefully conducted test is meaningless unless the specimen is representative of the material being tested. Accordingly, careful attention to sampling is a prerequisite for all tests.

Because of the nature of plastics, it is often difficult to select a truly representative sample. The amount of sampling depends upon the level of quality control required and must be agreed upon in advance by producer and consumer.

Sampling can be performed in various ways. In some cases, users select a random number of boxes or drums from a total lot and press individual test samples from each. At other times, samples are prepared by the manufacturer and testing is performed by either the manufacturer or user, or by both. The most common practice, however, is for the manufacturer to sample and test material after it has been processed through the extruder.

Most plastics undergo a change in workability between the time of manufacture and the time of installation and even with the best packaging methods, workability drops with time. Because of this, the product may become unsuitable for use if there is a long time lapse between manufacture and installation. Accordingly, workability is often checked on site. When users specify workability, the specification must state whether the value is to be measured at the place of manufacture or on site prior to installation.

On critical installations, sampling before and during installation is often required. These samples are used to monitor engineering properties, such as density, shrinkage, erosion resistance and strength.

Very little sampling is carried out on installed plastics and acceptance is usually based on

Table 3.4 -- Properties of Plastics and Ramming Mixes

Classification	Super Duty Heat Set	Super Duty Air Set	60%	80%	Phosphate-Bonded			
			Al ₂ O ₃ Heat Set	Al ₂ O ₃ Heat Set	50% Al ₂ O ₃	85% Al ₂ O ₃	90% Al ₂ O ₃	90% Al ₂ O ₃ Soft
Pyrometric Cone Equivalent, Cone #	33-34	33-34		38-39	---		---	---
Material Required, lb/ft ³	145	145	155	178	155	185	195	185
(ASTM C 491)								
Cold Modulus of Rupture, psi								
220 F (105 C)	40-80	225-350	155-255	150-225	960	800-1200	1600-2400	1100-1700
1500 F (815 C)	90-140	175-275	200-300	125-200	840	900-1400	2000-3000	1100-1700
2550 F (1400 C)		---	---		1980	1100-1700	1800-2700	1000-1500
(ASTM C 129)								
Permanent Linear Change, percent*								
<u>S</u> denotes shrinkage, <u>E</u> denotes expansion								
220 F (105 C)	0.3-0.7S	0.3-0.7S	0.4-0.8S	0.3-0.7S	0.1S	0-0.3S	0-0.3S	0-0.2E
1500 F (815 C)		---	---	0-1E	0.1S	0-0.3S	0-0.3S	0.15-0.1
2550 F (1400 C)	0.1S	0.1E	0.5S-0.5E	0.5-2E	0.5S	0-0.5S	0-0.5S	1-2E
(ASTM C 16)								
Hot Load Deformation, Percent at								
2640 F (1450 C)	5-8%		4-7%	1-3%	---		---	---
Chemical Analysis								
(Calcined Oxide Basis), Percent								
SiO ₂	50-53	48-51	32-35	11-15	38-42	6-9	2.5-3.5	4-6
Al ₂ O ₃	42-45	43-46	60-63	79-83	54-58	82.5-90	95-97	93-95
Fe ₂ O ₃	1-2	1-2	1-1.5	2.5-3.5	1-2	1-2	0.1-0.3	0.2-0.4
CaO	0.1-0.6	0.3-0.9	0.1-0.6	0.05-0.15	0.50-0.15	0.05-0.15	0.02-0.1	0-0.1
MgO	0.1-0.6	0.2-0.7	0.1-0.6	0.05-0.15	0.05-0.15	0.05-0.15	0.02-0.1	0-0.1
TiO ₂	1.5-2.5	1.5-2.5	2.5-3	2-3	1.5-2.5	1.5-2.5	0.02-0.1	0.1-0.3
Na ₂ O + K ₂ O	0.5-1	0.8-1.3	0.3-0.8	0.5-0.15	0.2-0.5	0.05-0.15	0.1-0.3	0.2-0.4
Pressed samples								

1 psi= 6895 Pa

Table 3.4 -- Properties of Plastics and Ramming Mixes (cont.)

Classification	Plastics Graphite				Ramming Mixes	
	Clay	60% Al ₂ O ₃	High Al ₂ O ₃	Al ₂ O ₃ Wet	90% MgO	Zircon Base
Pyrometric Cone Equivalent, Cone #	20-23	36-36	38-39	---		
Material Required, lb/ft ³	138	150	165	193	172	220
(ASTM C 491) Modulus of Rupture, psi						
220 F (105 C)	300-450	300-600	350-550	600-900	1000-1500	1200-1850
1500 F (815 C)	50-75	150-225	110-170	400-600	600-900	1100-1700
2550 F (1400 C)		---		900-1400	1000-1500	1600-2400
(ASTM C 129) Permanent Linear Change, Percent*						
<u>S</u> denotes shrinkage, <u>E</u> denotes expansion						
220 F (105 C)	0.6-1.2S	0.7-1.2S	0.4-.8S	0.3-0.6S	---	0.1-0.4S
1500 F (815 C)		---		0.4-0.7S	0-0.2S	0.1-0.5S
2550 F (1400 C)	0.55-1E	0.5-1.5E	0.55-0.5E	0-0.5S	0.1-0.3S	0.2-0.7S
(ASTM C 16) Hot Load Deformation, Percent at						
2640 F (1450 C)	---	3.6	1-2.5			2-4
2900 F (1600 C)	---	---	---	1-2.5	---	
Chemical Analysis (Calcined Oxide Basis), Percent						
SiO ₂	65-68	30-34	11-14	8-10	0.5-0.8	33-34.5
Al ₂ O ₃	25-28	59-63	81-85	89-91	0.05-0.15	1.5-2.5
Fe ₂ O ₃	0.5-1.5	1.5-2.5	1.5-2.5	0.2-0.5	0.05-0.15	0.1-0.2
CaO	0.8-1.4	0.3-0.8	0.05-0.2	0.05-0.15	0.5-0.8	Trace
MnO	0.1-0.6	0.1-0.6	0.05-0.2	Trace	97.5-98.5	Trace
TiO ₂	0.5-1.5	2-3	2-3	0.2-0.5		0.2-0.4
Na ₂ O + K ₂ O	2.5-3.5	1-2	0.1-0.3	0.2-0.5	0.5-0.7	0.5-0.8
ZnO	5-7	5-8	5-7		---	62.5-64
Pressed samples					1 psi = 6895 Pa	

on visual inspection. Cored samples are occasionally taken to evaluate the mechanical properties of a fired lining. These samples are taken using the same method used to core concrete.

3.6 -- Product characteristics

Table 3.4 lists product characteristics important to the selection of plastics.

3.6.1 Chemical and mineralogical analysis (ASTM C 572 to C 576 and C 705) -- The ASTM analysis procedures are primarily wet chemical techniques. The specific technique will vary depending on the raw material composition. The analyses are usually presented on a calcined basis and expressed as the oxide. The data are important for material selection, particularly resistance to acid and basic slags. Except where there are unusual conditions in the process environment, chemical composition is a factor in determining a product's utility.

In most laboratories, routine chemical analysis is done by x-ray fluorescence, (x-ray spectroscopy), atomic absorption and inductively coupled plasma (ICP) techniques. All of these techniques are rapid, accurate and permit multi-element analyses from the same sample. Mineral analysis is performed by petrographic, microscopic and x-ray diffraction techniques. In postmortem studies, the mineral analysis is often more important than the chemical analysis. This is because of the mineralogical changes that are likely to take place in service.

3.6.2 Sieve analysis (ASTM C 92) -- Almost all raw materials used in plastics and ramming mixes are characterized by their sieve analysis. Two types of sieves are available, Tyler and ASTM (U.S. Standard Series). The opening size of the two types of sieves is often different for the same number sieve and it is therefore important to specify the type to be used. Raw materials are often specified by size range or maximum particle size. For examples, “-100-mesh (Tyler)” means that at least 90 percent (by weight) of the material will pass the 100-mesh Tyler screen.

Sieve analyses run on wet plastics should follow the wet analysis procedure described in ASTM C 92. This procedure involves slaking the plastics in water prior to analysis and requires special care to ensure that de-agglomeration is achieved.

3.6.3 Type of set (bond mechanism) -- The setting characteristics describe the temperatures or other treatments needed for bonding. Typical descriptions include air-, heat-, and chemical set. Heat must be applied to some plastics containing a specified period after installation. This is to prevent moisture pickup and binder migration. Plastics containing concentrated phosphoric acid are an example of where this is important. Information regarding the bond and the proper treatment for developing optimum performance properties can be obtained from the manufacturer. A detailed description of binders used in plastic refractories is included in **Chapter 2**.

Dry vibratable mixes are unique in that the working face develops a bond on heating, but the material at the cold face remains as an unbonded granular material. During heating and cooling, this unbonded layer provides stress relief for the lining.

3.6.4 Service temperature limits (service range) -- The maximum service temperature is typically the first information required to determine a product's use. Factors affecting this

value are discussed in **Chapters 2 and 4**. The maximum service temperature of plastic is normally defined as the point above which unacceptable volume changes occur. It is about 150 F to 200 F (65 C to 93 C) below the actual softening point of the plastic (see **Section 3.6.5**).

Most manufacturers establish maximum service temperatures by testing products in clean, oxidizing atmospheres such as are present in furnaces fired with natural gas or heated by electric elements. If sufficient quantities of iron compounds are present in the plastic, a reducing atmosphere can lower the melting point and hence, the maximum operating temperature, by 100 F to 200 F (38 C to 93 C) (4).

Solid impurities from the fuel and/or process dusts which contact the plastic usually lower the maximum permissible service temperature. This is because the solid impurities react with the plastic to produce compounds having a lower melting point. At high temperatures, these compounds will melt and flow. This phenomenon is generally referred to as slagging or fluxing. The lower softening temperature of these new compounds defines the operating temperature for the installation. Solid impurities do not usually react to cause slagging or fluxing below about 2400 F (1315 C).

The chemistry of plastics in contact with molten glasses, fluxes and slags is important, and care must be taken to avoid wetting of the plastic and/or reaction between the plastic and contents. Improper chemistry can result in a reduction of the maximum service temperature.

Dry, heat-setting and some chemically bonded mixes require a minimum temperature to develop a bond. In product literature, this minimum temperature may be shown as “Minimum Vitrification Temperature” or as the lower temperature of “Service or Usable Range”.

3.6.5 Refractoriness (ASTM C 24) -- Refractoriness is frequently defined by the softening point or by the temperature at which a product will no longer support its own weight.

The refractoriness of plastics can be determined by measuring the material's Pyrometric Cone Equivalent (PCE). This technique compares the deformation of the test sample to deformations of pyrometric cones which have known associated refractoriness values. PCE standard cones bend at known specific temperatures when heated at specified rates. The heating rate is important and standard PCE cones will bend at higher temperatures when faster heating rates are used. Because of this, the temperatures listed in tables accompanying PCE numbers are for specific heating rates. PCE is useful for product classification. However, because products are rarely usable up to their reported PCE, the test value should never be used for establishing the maximum service temperature limit.

3.6.6 Density, specific gravity, porosity and permeability (ASTM C 20, C 134, C 357, C 493, C 830)--Raw materials used for plastics are granular and the densities can be determined by the procedures of ASTM C 357 or C 493. Because of their role in particle segregation, specific gravity and density are important in granular mixes. Segregation will cause serious variation of the composition and properties within the installed plastic.

The density of the fired plastic can be determined using the methods set out in ASTM C 20, C 134, C 357 and C 830. The in-service weight is sometimes shown on data sheets as the bulk density of the material after it has been dried and/or fired to service

temperatures. The bulk density of an unfired plastic can be determined by pressing (or ramming) the material into a known volume, measuring the weight and calculating the density.

Fired bulk density affects the specific heat of the lining and thus the lining's capacity to store and conduct heat. In addition, it can be used to estimate the relative thermal conductivity and the energy required to heat a lining. Bulk density also has value as a quality control tool.

Bulk density is primarily dependent on the density of the aggregates, but can also be affected by improper consolidation. For plastics, bulk density ranges from 100 to 215 lb/ft³ (1600 to 3450 kg/m³). The clay base compositions are in the 125 to 145 lb/ft³ (2000 to 2320 kg/m³) range. Increasing alumina content results in increased density up to 195 lb/ft³ (3130 kg/m³) for the maximum alumina value. The bulk density of zircon-base ramming mixes is typically in the 200 to 215 lb/ft³ (3200 to 3450 kg/m³) range. Within a given classification, ramming mixes generally exhibit higher densities than plastics and thus, are more resistant to erosion and slag attack.

The porosity of the installed plastic is particularly important because:

- (1) It controls the rate at which volatiles can be removed during curing and initial heat-up, and
- (2) It controls many refractory properties during use.

In some cases, calcined aggregates such as bauxite and fireclays contain significant open porosity. In water-based mixes this can be a factor in determining the water content needed for proper workability. Because this water is often tightly held by capillary action, it can also be a factor in dry-out. It should be noted the porosity changes considerably during drying, heat-up and use. Generally, porosity decreases during curing, increases rapidly during heat-up, and decreases as the ceramic bonds form and sintering takes place at operating temperatures.

The apparent porosity of most plastics is approximately 15 to 25 percent after firing. However, the porosity may be as low as 10 to 15 percent in dense, extra-high alumina ramming mixes.

The permeability of plastic refractories varies greatly and depends on the aggregates involved, the product type and the installation technique. Permeability of fired plastics at 1500 F (815 C) is typically two to three times the value after drying.

Air permeabilities of test samples fired to 1500 F (815 C) range from 1.2 to 50 centidarcies.

3.6.7 In-situ material requirements -- Data sheets for monolithic plastic linings show considerable variation in defining the amount of material required to fill a given in-situ volume. Terms such as weight to place, installed density, amount required and amount required as rammed, are common in the industry. The net amount of material required for the lining can best be determined by using the installed bulk density figure. This is commonly expressed in pounds per cubic foot (lb/ft³) or kilograms per cubic metre (kg/m³).

3.6.8 Moisture content -- Normally, moisture content is only supplied for wet ramming mixes. For plastics, which require the addition of a liquid, the required amount is specified by the plastic manufacturer.

A low moisture content is necessary for applications such as induction furnaces, where

rapid heating cannot be avoided.

3.6.9 Workability (ASTM C 181) -- Workability index is the primary property used to differentiate between plastics and ramming mixes. Plastics exhibit workability indices in the range of 15 to 40 percent, while ramming mixes generally have workability indices less than 15 percent. ASTM C 64 (Standard Specification for Refractories for Incinerators and Boilers), which was withdrawn as an ASTM standard in 1984, required a 15 to 35 percent index for plastic refractories. Plasters and mortars usually have a higher workability than plastics.

The workability index is determined by measuring the plastic deformation of a molded test specimen when subjected to impact. Fireclay and high alumina plastic refractory specimens are molded by compaction in a steel cylindrical mold according to ASTM C 181. Sometimes, the number of impacts and equipment required to achieve the desired density and a stress-strain curve of the green compact are used as additional data for evaluating the relative workability.

Workability and moisture content provide a basis for judging loss of workability when the storage life of the plastic is approached.

3.7 -- Engineering properties

The engineering properties of plastics vary with temperature. Accordingly, it is important to determine these relationships. Because the adjacent lining elements prevent the free unrestrained movement of the lining, temperature and stress distribution calculations are approximate unless advanced stress analysis methods are used. Test specimens are generally heated on all sides. Accordingly, the engineering properties and mechanical behavior of laboratory test samples are significantly different from those of field applications.

Advanced stress analysis techniques, such as the finite element method, are finding increasing acceptance for the design of refractory installations. However, these methods are only as good as the input data and accurate, temperature-dependent, engineering properties are essential if meaningful results are to be obtained. Refractories manufacturers are aware of the need for this data and are developing the necessary tests. In addition, they are beginning to publish the engineering properties of their proprietary plastics at temperature and as a function of previous thermal exposure.

Discontinuities may also exist through the thickness of the lining. For example, dry vibratables develop bonded refractory characteristics at and near process temperatures, but remain loose and unbonded in the lower temperature regimes away from the working face. If differential linear change is excessive, shear planes can develop and cause disruption of the lining integrity.

Many engineering properties are published in manufacturers' literature. Unlisted properties are sometimes available upon request. However, not all data has been generated and it is sometimes necessary to develop the required technical information.

Table 3.4 lists physical properties typically found on data sheets. It should be noted that, in order to minimize variability due to forming, many of these properties are determined on laboratory pressed specimens. Rammed specimens and actual field linings

will generally exhibit lower densities, higher shrinkages and lower strengths compared to the pressed specimens.

3.7.1 Dimensional change -- Linear change may be either positive (expansion) or negative (shrinkage). The total linear change is created by two independent effects referred to as permanent linear change and reversible thermal expansion.

3.7.1.1 Permanent linear change (ASTM C 179)-- Drying and firing shrinkage occurs in all monolithic plastic installations. The measured test value is used to predict the permanent dimensional changes which take place during drying and firing. If shrinkage is not taken into account, the installation will undergo excessive cracking and reduced service life. This is especially important when anchors are present because they tend to be sites of high stress concentration and points of crack initiation.

Drying and firing shrinkage is normally determined according to the procedures of ASTM C 179. The test calls for pressing plastic refractory in a 9 x 4.5 in. (225 x 113 mm) mold to approximately 2.5 in. thickness with sufficient pressure [about 1000 psi (6.9 MPa)] to produce a uniform structure without voids. The length of each specimen is measured immediately after pressing, after drying and cool-down to room temperature, and after firing and cool-down to room temperature. The dried and fired shrinkages (expansions) are calculated as percentages of the original pressed lengths and are known as the permanent linear change. Most of this change occurs during the initial heat-up and is caused by water loss at low temperature and glass formation at high temperature.

It is important to note that field installations are normally rammed rather than pressed and that field shrinkage will be significantly more than laboratory measured values. In general, shrinkage of pressed samples will be about half that of field rammed materials.

Prior to being withdrawn, ASTM C 64 limited the combined shrinkage due to drying and 2910 F (1600 C) fired to 2.5 percent for super-duty fireclay and high alumina plastic and to 3.0 percent for drying and 2750 F (1400 C) firing for high duty plastics.

Combined shrinkage of commercial plastics seldom exceeds 1.5 percent. Many exhibit an overall expansion on heating, some in excess of 5 percent. This expansion ensures a tight structure at operating conditions. In large sections, permanent shrinkage results in small cracks at approximately every 30 to 40 in. (750 to 1000 mm). The cracking generally occurs during drying and, because of thermal expansion (see Section 3.7.1.2), the cracks normally close at elevated temperature.

3.7.1.2 Thermal expansion -- Thermal expansion is the change of volume that occurs as a material is heated. It is reversible and is defined as the recoverable change per unit length that occurs solely as a result of heating. On cooling, the specimen returns to its original length unless permanent linear changes have occurred.

The net linear change of a plastic or ramming mix at a given temperature is the sum of the reversible linear expansion at that temperature, and the permanent linear change corresponding to the highest temperature to which it has been heated. **Figure 3.7.1.2** shows typical length changes due to both permanent linear change and reversible thermal expansion.

There is no standard test for thermal expansion, even though it is an important engineering property of plastics. The closest standard is ASTM C 832 (see **Section 3.7.2.3**). Most laboratories measure thermal expansion using a heating rate of 1 deg C/min. This test

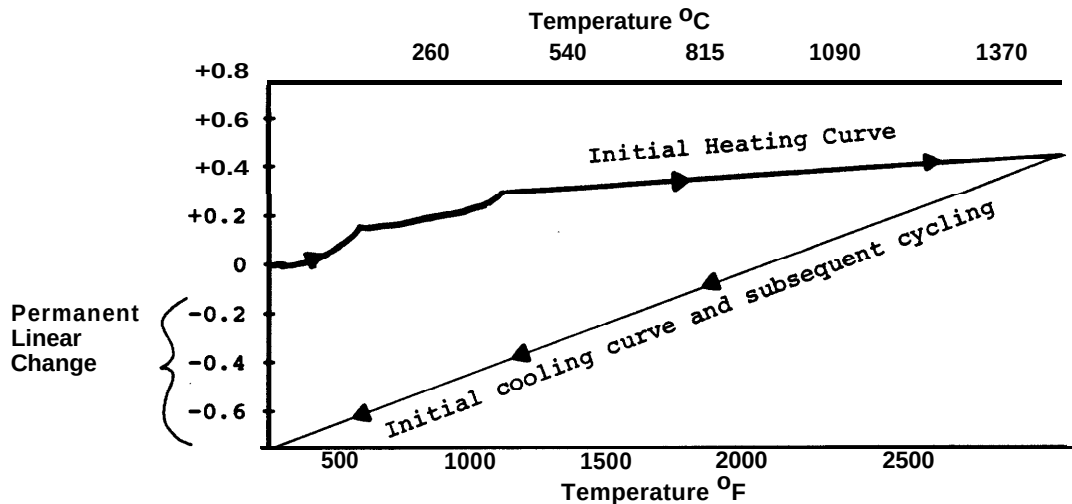


Fig 3.7.1.2--Net thermal expansion of a typical super-duty plastic refractory

allows calculation of the overall expansion coefficient and a measure of irreversible expansion, if present. In addition, thermal expansion will identify any polymorphic phase transitions present and quantify the magnitude of the associated volume changes.

3.7.2 Mechanical strength and structural stability -- Strength data and related structural stability properties (creep, thermal expansion under load and hot load subsidence) are obtained using various ASTM methods. Representative values of some of these properties are in [Table 3.4](#).

Fig. 3.7.2 shows typical relationships between temperature and strength. As noted previously, strength values obtained from pressed specimens are generally higher than those from in-place linings or from laboratory rammed specimens. Specimen cross sections must be large enough to accommodate the largest aggregate particles and to minimize defects due to forming.

3.7.2.1 Cold strength (ASTM C 133, C 491) -- Cold crushing strength (ASTM C 133) and room temperature modulus of rupture (ASTM C 491) tests are widely used to determine the strength of dried and fired plastic refractories. Like all ceramics, the strength measurements vary from sample to sample and results must be treated statistically.

Data obtained on specimens heated to a specific temperature, heat soaked, totally immersed in the furnace atmosphere and cooled to room temperature, are generally specified as cold strength. The data obtained from these tests is only meaningful if the maximum exposure temperature is below that where significant fluxing or glass formation occurs. Glass development above 1500 F (815 C) causes misleadingly high strengths to be obtained at room temperature. This is because of the solidified glass bond which is very strong at room temperature. As the glass bond softens, strengths at operating temperature drop significantly.

3.7.2.1.A Cold compressive strength (crushing) -- Cold crushing strength (CCS) data

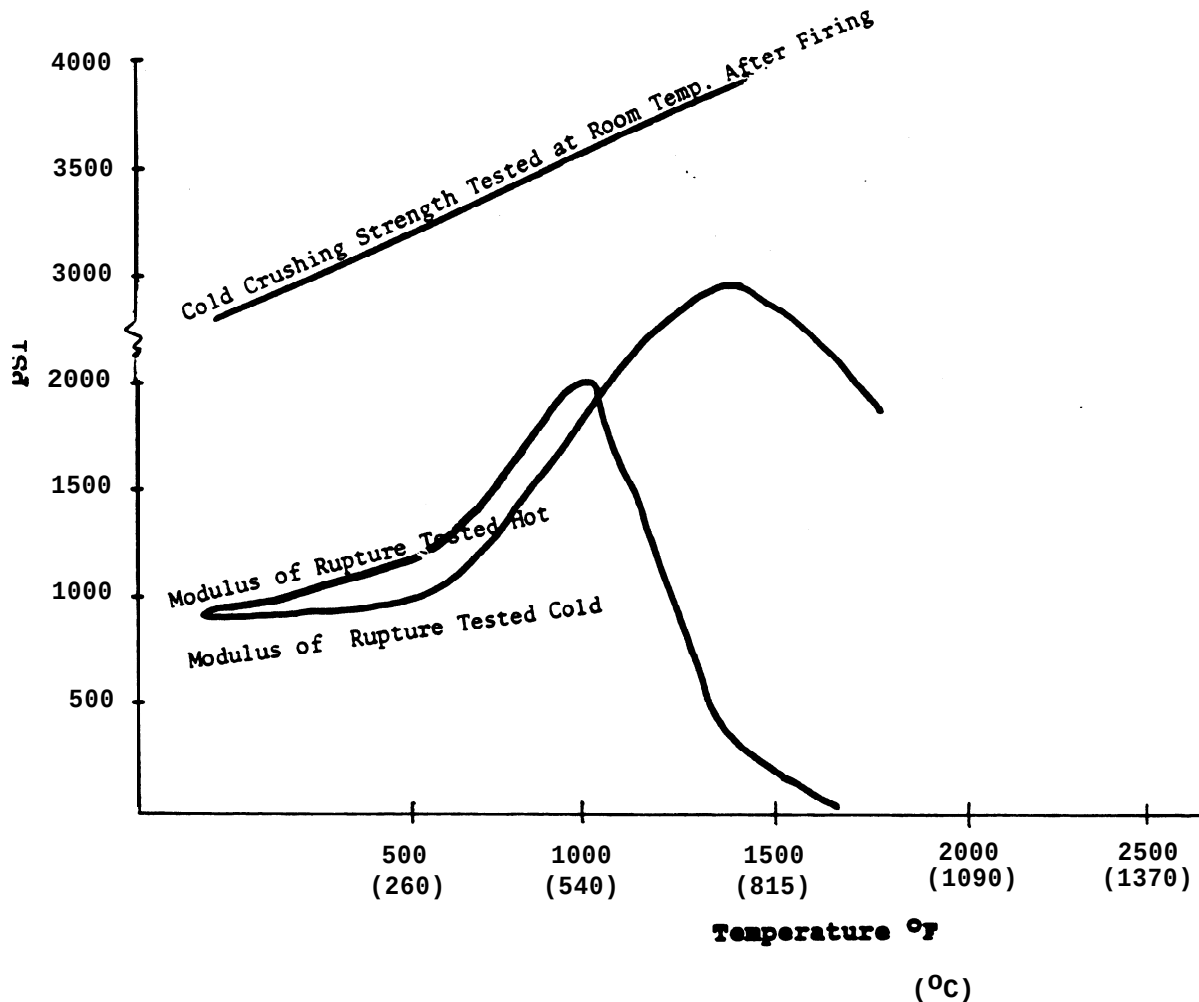


Fig. 3.7.2--Effect of temperature on the modulus of rupture and cold crushing strength of an 85 percent alumina phos-bonded plastic refractory (1 psi = 6895 Pa)

varies greatly with the size and geometry of the specimen. For valid comparison of results between materials, specimens must have identical geometry and size and must be tested in the same orientation relative to the forming pressures. Typical specimen sizes are 9 x 4.5 x 2.5 in. (225 x 113 x 63 mm) with the load applied on the smallest surface (ASTM C 133), 2 in. (50 mm) cubes and 3 in. high x 2 in. diameter (75 x 50 mm) cylinders. Strength values vary with such factors as size and shape of test specimen, method of loading, degree of flatness, firing temperature, padding materials and cut and uncut surfaces.

CCS values are generally three to six times the value of the cold modulus of rupture

(see Section 3.7.2.1.B). The main use of CCS testing is for quality control and the data are not used widely for lining design.

3.7.2.1.B Cold modulus of rupture -- The modulus of rupture (MOR) obtained from a flexural test (ASTM C 491) is a measure of tensile strength. The cold MOR test is run at room temperature using specimens that have been heated to specific temperatures and then cooled. The MOR for plastics may be as low as 40 to 50 psi (0.28 to 0.34 MPa) after drying at 230 F (110 C). However, the value increases to 1000 to 3000 psi (6.89 to 20.7 MPa) on firing. Dry ramming mixes and vibratables have essentially no dry strength but after firing develop good strength on the working face. Moist ramming mixes are generally stronger after firing than the plastics, with some reaching an MOR value of 5000 to 5500 psi (34.5 to 38.0 MPa). The binder and aggregate have a major influence on the strength of a plastic, which is also affected by the method of forming and the heat treatment.

3.7.2.2 Hot strength (ASTM C 583) -- Strength measurements made at elevated temperatures (where glass formation and mineralogical changes occur) are more meaningful than measurements made at room temperature after firing.

3.7.2.2.A Hot modulus of rupture -- The hot modulus of rupture (MOR) test (ASTM C 583) is conducted at operating temperature. The test eliminates the strengthening effect of glass, which is soft and viscous at high temperature, but hard and brittle at room temperature. The refractory industry is tending to adopt this test in place of cold MOR. The test specifies a 1 in. (25 mm) square bar. However, 2.5 in. (64 mm) bars are more applicable to plastics than 1 in. (25 mm) bars because defect-free specimens can more readily be formed. This is particularly important when large size aggregates are used. Typical test temperatures are 1000 F (540 C), 1500 F (815 C), 2000 F (1095 C), 2300 F (1260 C), 2500 F (1370 C) and more recently, 2650 F to 2700 F (1454 C to 1482 C). This data more accurately reflects the in-service strength of the refractory and takes proper account of the physical transformations and liquid phase formation. The availability of hot MOR data is limited, but this situation is expected to change as hot MOR becomes recognized as the primary strength measurement for refractories.

3.7.2.3 Thermal structural stability (ASTM C 832, C 16) -- The ability of refractories to withstand stress-induced deformation at elevated service temperatures is important.

The structural stability of a lining is affected by phase changes, by the amount and viscosity of the glass developed, and by the load on the lining. This property can be evaluated by using one or more of the following ASTM tests:

C 832--Measuring the Thermal Expansion of Refractories Under Load

C 832--Creep

C 16--Hot Load Subsidence

ASTM C 832 is an important aid in characterizing the performance of plastics on initial heating, with and without load. Deformation during initial heating is valuable in identifying temperatures at which chemical reactions, phase changes, liquid formation and creep deformation occur.

Very little information is available on creep of plastic refractories. However, its importance to the refractory designer is now recognized and the necessary

being generated using the recently issued (1982) ASTM C 832 procedure. This method is also used to determine thermal expansion under load. Creep data is important to the designer or structural components and provides an indication of refractory lining performance and integrity.

Hot load subsidence (ASTM C 16) measures plastic deformation under a given heating schedule and load. Frequently, this test is run under a 25 psi (0.17 MPa) uniaxial compressive load, with a 1.5 hour hold at either 2460 F (1350 C), 2640 F (1450 C) or 2900 F (1595 C). Hot load testing is less expensive than developing creep data and provides a relative measure of stress-induced deformation on heating. Even though there is no accepted limit for deformation under the hot load subsidence test, it is a useful test for quality acceptance.

Hot load subsidence and creep data, together with hot MOR and permanent linear change data are often used to set the upper use limit of the plastics. The data are also used for classification and specification purposes.

3.7.3 Modulus of elasticity and stress-strain properties (ASTM C 885) -- ASTM C 885 can be used to measure modulus of elasticity of plastics. Only a limited amount of data is available with values ranging from 1×10^6 psi (6.89×10^3 MPa) to 8×10^6 psi (55.12×10^3 MPa).

The small amount of available data suggests a correlation between elastic modulus and strength. The modulus of elasticity is dependent on the type and degree of bonding developed on firing. As with strength data, the values obtained from prefired specimens tested at room temperature are higher than those obtained at temperature.

As discussed previously, there is a growing demand for engineering property data as a function of temperature. For finite element analysis, stress-strain curves at temperature are particularly important. At present (1984), test methods to obtain this data have not been standardized. However, the data are now becoming available and are being used for design.

3.7.4 Permeability (ASTM C 577) -- In some cases, the rate at which gases can flow through a monolith is important. ASTM C 577 measures this property at room temperature using prefired plastic specimens. As with other properties, the permeability of plastics changes during drying, heat-up and service. Excessive cracking in the installation will greatly increase the permeability and make the permeability test data much less meaningful.

3.8 -- Thermal properties

3.8.1 Specific heat -- The specific heat of a material is the ratio of the heat capacity of the material to that of water. It is an important property which controls the energy required to raise the temperature of a material.

Current practice is to measure the specific heat by the drop method. With this method, a sample is equilibrated at a known temperature and then dropped into an insulating calorimeter. From the change in temperature in the calorimeter, the heat capacity can be calculated. Provided the test is performed properly, measurements made by this technique are very accurate.

Another technique gaining popularity involves use of a differential scanning calorimeter (DSC). The DSC technique is a dynamic measurement that compares the heat required to

raise the temperature of a known weight of a particular material to the heat required to raise the temperature of a known weight of a standard material. This technique is less accurate than the drop method, but is much faster.

The specific heat of fired plastics increases with temperature. Typical values range from 0.20 Btu/lb/F (837 J/kg/C) at 100 F (38 C) to about 0.29 Btu/lb/F (1210 J/kg/C) at 2500 F (1370 C). These values can vary ± 0.025 Btu/lb/F (100 J/kg/C), depending on the aggregate.

3.8.2 Thermal conductivity (ASTM C 201, C 417)-- The thermal conductivity, k , of a material is a measure of the rate of heat transfer through a sample under a thermal gradient. Because of this, the thermal conductivity is important in establishing the heat loss through a refractory lining. For conditions of steady state, where both the rate of heat flow and the temperature are independent of time, the heat flow per unit time, q , between any two points is given by:

$$q = kA \cdot \Delta T / \Delta X$$

where A is the cross sectional area (measured perpendicular to the direction of heat flow) and $\Delta T / \Delta X$ is the temperature gradient between the two points. For situations in which either the heat flux or temperature gradient vary with time, the heat flow per unit time through the material is known as the thermal diffusivity, α , and is given by:

$$\alpha = k / \rho C_p$$

where ρ = density of the material, and

C_p = heat capacity at constant pressure.

ASTM method C 417 is used to measure the thermal conductivity of unfired refractory monoliths, such as plastics. This particular test is one of several ASTM test methods for determining the thermal conductivity of refractories. Thermal conductivity varies with temperature and, for this reason, conductivity values should be obtained at actual lining temperatures in the intended service.

It should be emphasized that the basic ASTM test method requires that steady state conditions be attained in the test system. Because attainment of a steady state heat balance is usually quite tedious, there are several non-steady state techniques in use. Some of these, such as the hot wire and laser flash diffusivity are described in Chapter 9. With these methods, thermal conductivity is calculated from thermal diffusivity values assuming known sample density and heat capacity at constant pressure. These non-steady state techniques have not, as yet, been adopted by ASTM.

For normal weight plastics, thermal conductivity tends to vary with density and the type of aggregate. **Figure 3.8.2** shows typical values (k factors) which range from about 4 Btu/in./ft².h.F (62 W.cm/m².h.C) for 125 pcf (2020 kg/m³) density material to about 18 Btu/in.ft².h.F (259 W.cm/m².h.C) for 175 pcf (2800 kg/m³) material.

3.9 -- Thermal shock and spall resistance

Plastics are generally more resistant to thermal shock than refractory brick and refractory castables, and practically all plastics will withstand repeated quenches through several hundred degrees. However, prolonged or extreme temperature cycling will result

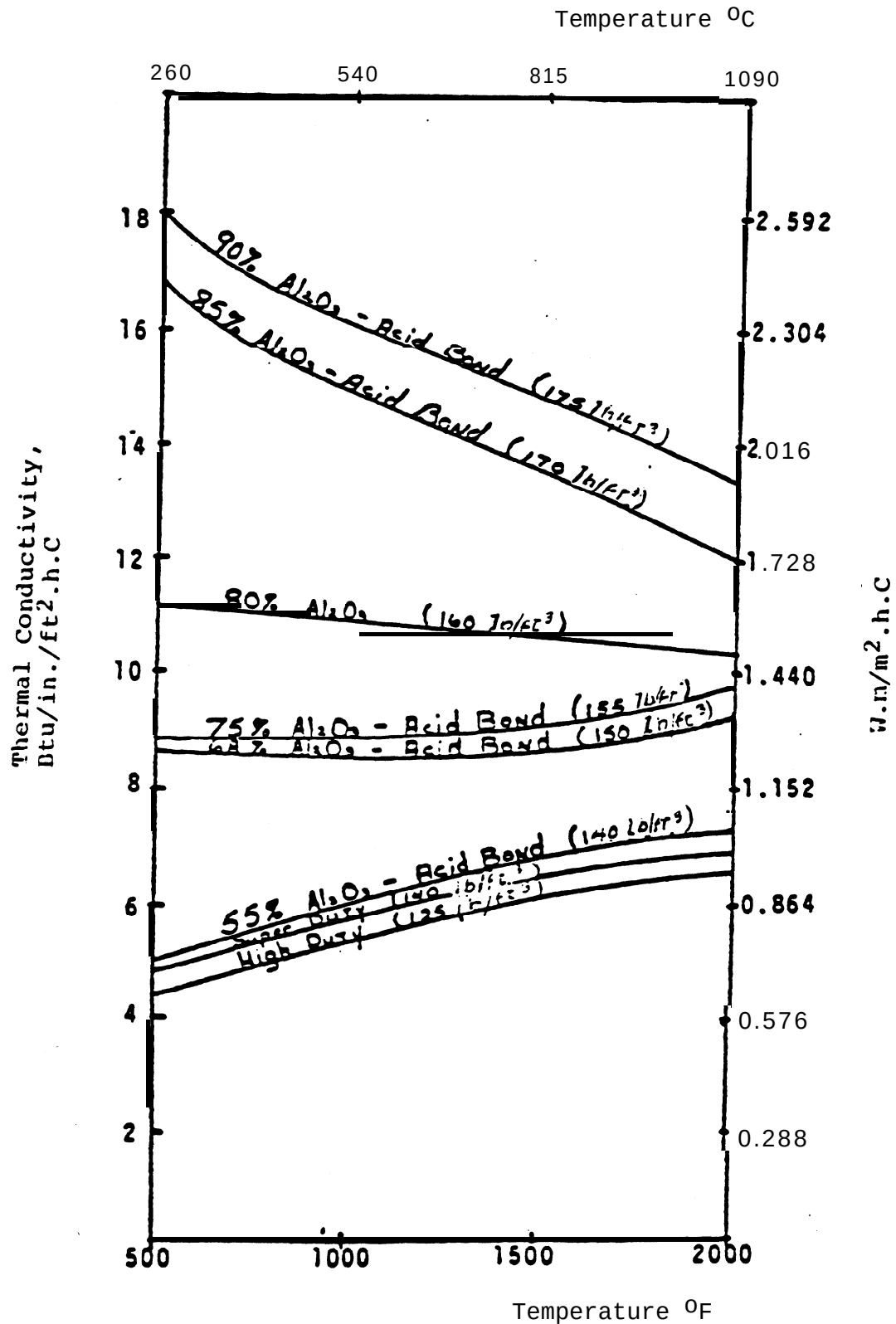


Fig. 3.8.2--Thermal conductivity of various plastic refractories (1 lb/ft³ = kg/m³)

in damage and eventual destruction due to cracking and spalling. ASTM C 180 (Standard Method of Panel Spalling Testing Fireclay Plastic Refractories), which was withdrawn by ASTM, specified a test procedure in which the specimens are prefired at 2910 F (1600 C) or 3000 F (1650 C) to promote ceramic bonding, and then subjected to thermal cycling. The material loss, which occurs primarily in the hot face area is measured and compared for different materials. The test is prescribed for high-duty and super-duty plastics only. Spalling loss by the 2910 F (1600 C) and 3000 F (1650 C) panel spalling test is generally in the range of 0 to 4 percent.

The panel spall test is expensive to run and was not favored by the refractories industry. More meaningful tests have been developed which are applicable to a wider range of materials. Two alternate approaches are discussed in [Section 9.4.2](#).

3.10 -- Electrical resistivity

Electrical resistance of plastics is important in electric furnaces and in other areas requiring electrical insulation at high temperature. Plastics, except those containing carbon or graphite, have very high resistivities at low temperature. The resistance decreases rapidly as the temperature increases. There are no standard test methods for measuring the electrical resistivity of plastics. However, the apparatus used in ASTM C 483 and ASTM D 1829 can be adapted for these materials. Both test procedures measure the resistivity of the specimen placed between two electrodes. The electrodes are either in direct contact with the specimen, or make contact through highly conductive iron filings. The results are reported as either total resistance or volume resistivity, p , in ohm-centimeters, as follows:

$$p = (A/h) R_v$$

where:

R_v = Measured total volume resistance

h = Average thickness of specimen in area covered by electrodes, mm

A = Area covered by the electrode, mm²

Electrical resistivity is very high for thoroughly dried plastics, but decreases with increasing temperature. Typical values are 11 to 16 megohm.cm at 900 F (480 C) and 0.005 to 0.01 megohm.cm at 1800 F (980 C). Acid-bonded plastics generally have lower electrical resistivity than air- or heat-setting plastics.

3.11 -- Abrasion/erosion resistance (ASTM C 704)

There is considerable confusion about the meaning of the terms abrasion and erosion when applied to refractories. ASTM defines abrasion of refractories as the “wearing away of refractory surfaces by the scouring action of moving solids.” Unfortunately, some in the refractories industry call this mechanism “erosion,” particularly if the moving solids are in the 40 to 500 micron size range.

Using the ASTM definition, the standard test method (ASTM C 704) for abrasion resistance at room temperature measures the volume of material abraded from a flat

surface when 1000 g of graded silicon carbide (SiC) grain are blown perpendicular onto the surface by air at 65 psi (0.45 MPa). The standard test covers samples made from plastics, castables and brick. The abrading media is No. 36 SiC with most particles in the 200 to 850 μm size range (sieve Nos. 20 to 70). This test provides an index for comparing the abrasion resistance of various types and brands of plastics. The data is presented as volume lost, which is calculated by dividing the weight loss by the specimen's bulk density.

The important factors affecting abrasion of plastics are, velocity of the abrading particles, particle size, impingement angle and temperature (both firing temperature and test temperature) (5,6). For operating temperatures below 1500 F (815 C), an abrasion test of prefired specimens at room temperature is a satisfactory and valid test. For operating temperatures above the liquid phase formation temperature of approximately 1500 F (815 C), the solidified glass will give misleading data from prefired specimens at room temperature.

The test data is generally taken at room temperature after soaking the sample at 1500 F (815 C) for 5 hours and then cooling. A test carried out at 1500 F (815 C) with no cooling shows no significant change in abrasion value when compared to the cold test.

Ramming mixes are generally more abrasion resistant than plastics, but some plastics have abrasion values as low as 400 to 500 mm^3 loss, which is typical of the better ramming mixes.

As discussed in [Section 9.4.1.2](#), field erosion testing is sometimes used as a nondestructive test of unfired plastics.

3.12 -- Resistance to carbon monoxide (ASTM C 288)

When plastics are used at low temperatures under reducing conditions, the possibility of disintegration exists. The deterioration occurs when carbon monoxide decomposes and forms elemental carbon deposits in the pores of the plastic. This results in bursting and disintegration of the plastic. The condition occurs near 840 F (450 C) and is accelerated by iron and iron compounds. ASTM C 288 requires special equipment and may require an exposure time of greater than 1000 hrs.

3.13 -- Resistance to slag attack (ASTM C 768)

Slag attack is caused by solution of the plastic in a corrosive slag liquid. The solution process depends upon the temperature, the composition of the slag, the composition of all phases in the refractory and the pressure and composition of the furnace atmosphere.

Slag attack is of major importance in many refractory applications and a number of test procedures have been developed which are suitable for measuring the ability of plastics to resist this attack.

3.13.1 ASTM procedures -- ASTM C 768 is a standard test for refractory brick at high temperature. The procedure can also be used for plastics and provides a measure of the relative resistance of plastics to the action of molten slag dripped continuously onto test specimens within a heated furnace. The equipment and procedure for this test is based on an article by McMullen (7). The slag is prepared in the form of preformed rods and is dripped onto a 3 in. (75 mm) thick refractory sample heated to the test temperature. Following complete melting of the slag rod, the depth, width and volume of the slag cut

in the plastic specimen are reported.

3.13.2 Static tests (8, 9, 10, 11) -- Cup tests and pencil tests are static slag tests which compare the resistance of plastics exposed to slag. The simplest cut test uses a plastic brick-type specimen drilled with a closed-end hole. The hole is filled with crushed slag and heated. Upon cooling, the specimen is sectioned and the reaction zone examined microscopically. In some cases, the slag is drained before the specimen is cooled.

Pencil tests use a cylindrical specimen inserted into a slag heated in an appropriate crucible.

Static slag tests provide useful information. For example, preferential solution of one phase can often be detected. The results of static tests must be treated with caution as there are several disadvantages. If the quantity of slag is too small, the composition can change during the test. Similarly, if the slag becomes saturated with the plastic, the corrosion rate can diminish. In addition, small crucibles do not usually develop convection currents and natural or forced convection considerations are often overlooked.

Static tests are used primarily as comparison tests of plastics or slags.

3.13.3 Dynamic tests -- Dynamic tests are the preferred method for evaluating the resistance of plastics to slag attack. In such tests, slag flows intermittently or continuously across the plastic. This removes the reaction products and prevents the slag from becoming saturated with corrosion products and the plastic constituents.

3.13.4 Other slag tests -- A number of coal gasification processes create a liquid coal-ash slag and the reaction of this slag with a number of refractory materials has been studied (12, 13). For some of this work, a large scale slag-corrosion test furnace was constructed with a cylindrical chamber using 9 in. (225 mm) brick of the candidate refractories. The rotary motion of the 3 in. (75 mm) deep and 25 in. (635 mm) diameter slag bath was created by the flames from three burners oriented to fire tangentially to the circumference of the bath. The tests were conducted at temperatures of up to 1500 F (815 C), for up to 500 hrs. The equipment and procedure permitted a relative ranking of a variety of refractory materials resistance to attack by coal-ash slag.

3.14 -- Status of testing procedures for plastics

At this time, the standardization of tests for plastics is not well established. Most of the tests were originally developed for burned refractory brick and are of marginal value for plastics. Many of the tests do not adequately represent the service conditions and new test procedures are needed. A number of refractory companies are in the process of developing such tests and it is anticipated these improved tests will lead to more realistic methods of assessing the in-service performance of plastics.

CHAPTER 4 -- CRITERIA FOR SELECTION

4.1 -- Introduction

Refractories are construction materials that are expected to perform satisfactorily in environments that usually include elevated temperatures and frequently include corrosive and erosive solids, fluids and gases, and mechanical and thermal shock from rapid heating