

2100 Material Selection Considerations

Abstract

This section introduces you to refractory lining materials and gives guidelines for choosing the type of refractory material to use. These guidelines include preliminary considerations (heat loss, the amount of time allowed for installation, economic factors, and previous history of this and similar linings) and refractory property considerations (thermal conductivity, erosion resistance, and temperature limits/shrinkage, strength, thermal expansion, resistance to thermal shock and chemical attack.) The use of additives to improve performance is also discussed. Typical failure mechanisms are listed, and factors used to develop a list of recommended brands are also named.

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2110 Refractory Basics

2111 Definition of a Lining System

Refractory lining systems are installed on the insides of vessels, lines and heaters to protect surfaces from aggressive service conditions such as oxidation, erosion, corrosion and heat damage.

A lining system includes the refractory material and the hardware that holds refractory material in place (anchorage). The type of refractory material, anchorage and operating conditions will dictate what other items the system will include and what method of installation will be used.

All parts of the lining system, including installation methods, must be correctly specified and the installation methods properly followed to obtain a satisfactory result. For this reason, inspection and testing are very important.

Definition of Terms

The following terms, used throughout the text, are defined here for easy reference:

Anchorage: the hardware that holds refractory material in place.

Back-up layer: in a two-component (two-layer) lining, the refractory layer nearer the shell.

Gas bypassing: process gas flowing between the refractory lining and the shell. The result is a hot spot on the shell.

Hot face layer: In a two-component (two-layer) lining, the layer on top of the back-up layer, exposed to high temperatures. It is stronger and more erosion-resistant than the back-up layer.

K factor: thermal conductivity expressed in Btu in./ft² hr °F.

Metal fiber reinforcement: stainless steel needles added to monolithic refractory materials for improved toughness and durability.

Modulus of Rupture (MOR) tests: flexure strength tests. Tests that determine the strength required, in psi, to bend a sample until it breaks.

Monolithic refractory systems: lining systems having no joints. They are gunned, cast, rammed, or vibration-cast in place. Because firebrick and refractory ceramic fiber modules and blankets have joints, they are not considered monolithic.

One-shot lining: a gun-applied semi-insulating castable lining, typically 4 or 5 inches thick.

Permanent Linear Change (PLC): measurement of shrinkage in monolithic refractory materials.

Rapid fire additive: organic fibers added to monolithic refractory materials to minimize explosive spalling during dryout.

Refractory concrete: a high-temperature cement proportioned and mixed with an aggregate; used for linings in refinery vessels and lines.

Service layer: same as hot face layer.

Spalling: the fracture or breakage of refractory material resulting from excessive stresses imposed by a sudden temperature change.

Two-component lining: a lining made of two layers: back-up and hot face.

Vapor barrier: high-temperature coating applied to the shell to protect against corrosion from condensed gases.

Vapor stop ring: a ring attached to a vessel's metal shell to block the path of high-pressure process gases that burrow behind the lining (gas bypassing).

Working lining: same as hot face layer.

2112 Types of Refractory Materials

The main types of refractory materials (in order of importance) for refinery/ petrochemical use are: castables, refractory ceramic fiber (RCF), plastics and brick. Some of these materials are better suited for certain services than for others. They also vary in cost, ease of installation, serviceability, and installation method.

Castables

The word “castable” is a general term for refractory concretes composed of an aggregate and a binder that are mixed together with water. Castables are hydraulically bonded by cement-water reactions or chemically bonded. New low moisture castables develop very high strengths through hydraulic bonding. Some of these materials are replacing older two-component linings because they both insulate and resist erosion.

Aggregate. The aggregate usually accounts for 60 to 80% of the volume of the finished product and is generally a pre-fired mineral product. Broken firebrick, calcined clay, bloated shale and expanded volcanic ash are commonly used aggregates. Very expensive aggregates, such as tabular alumina, fused cast granules, and silicon carbide are used where severe service conditions exist.

Binder. The binder is usually some type of calcium aluminate cement. The hydraulic cements commonly used in refractory materials work by reacting with water to form hydrated calcium aluminate phases that set into a rock-like mass. Some castables also contain chemically-setting binders such as phosphates and silicates.

Three types of calcium aluminate cements are used in castables. They are generally classed as low-, intermediate-, and high-purity.

- Low-purity cements (e.g., Ciment Fondu and Lumnite) are the most widely used, and of course, the least expensive. They are used in most standard-weight and insulating castables where the higher temperature limits and/or low iron contents of the other cement types are unnecessary.

- Intermediate-purity cements (also called “low iron” cements; Refcon is an example) are used in naphtha reforming units to guard against catalyst poisoning and in applications where carbon monoxide might disintegrate the refractory lining [11].
- High-purity cements (such as CA-25 and Secar 71) are the most expensive. They are found in castables where superior heat resistance and/or higher bonding strengths are needed. Examples include castables rated for 2800°F and higher, erosion-resistant castables, products formulated for vibratory casting, and low silica castables (such as those used for secondary reformer linings).

Figure 2100-1 shows chemical analysis and some physical property ranges for the three types of commercial cements. Specific gravity generally ranges from 2.95 to 3.25 with the higher values in the low and intermediate purity cements, reflecting larger amounts of Fe_2O_3 .

Fig. 2100-1 Chemical Analysis Ranges for Three Types of Commercial Cements (binders)

	Low Purity	Intermediate Purity	High Purity
Al_2O_3 (ASTM C-573) - %	36-47	48-62	70-80
Fe_2O_3 (Total Iron) - %	7-16	1-3	0.02-0.2
CaO - %	35-42	26-39	18-26
SiO_2 - %	3.5-9.0	3.5-9.0	0-0.5

Cement colors range from black to white depending on the amount and form of iron oxides, with low purity grades being black to dark gray if reduced or light brown if oxidized, intermediate purity grades being light gray if reduced or tan if oxidized, and high purity grades being white.

The physical properties of the finished castable are the result of the combined effects of the aggregate and binder. For example, castables containing a binder of portland cement often used in construction concrete (mainly calcium silicate) should not be used at temperatures above 800°F due to their inherent instability with temperature cycling.

The proportions of cement and water used in the castable mixture also affect the finished product. Low-cement castables have improved strength and shock resistance. Low-moisture castables are particularly suited for installation by vibration casting. Many, but not all, low moisture castables are also low cement.

Other Parts of Castable Lining Systems. Castable lining systems often include: metal fiber additive (to minimize cracking and spalling), expansion and contraction joints (to control cracking during heating and cooling), and vapor stop rings.

See Sections 2200 and 2500 for more information on use and installation of castables. See also IRM-MS-4785, -4786, -4787, and -4788.

Refractory Ceramic Fiber (RCF)

This material is essentially a high-temperature form of the fiberglass material used in home insulation. The word “refractory” is used to distinguish RCF from the more conventional, low-temperature fiber. RCF is used in both modular and fiber wall (blanket or board) form. Common trade names are given in Section 2300.

Manufacturers make modules either by “folding” or stacking strips of this material in blanket form into 12-inch squares that are about 6 to 8 inches thick. Each module is strapped to keep it compressed until after it is installed. Because they are compressed, the modules shrink very little and also resist moderate gas velocities and erosion. These features are causing modules to gain popularity as the lining system of choice for heaters.

Fiber wall is a combination of layers of refractory fiber blanket impaled on anchors. The blanket comes in rolls about 1 inch thick and 24 inches wide. This system is an acceptable approach in lining heaters and other heat enclosures when operating conditions, particularly temperature and erosive particles, are moderate. There are other forms of RCF, such as board, bulk fiber, vacuum-formed shapes and sprayable RCF.

See Sections 2300 and 2600 for more information on use and installation of RCF. See also IRM-MS-4789 for installation, and IRM-MS-4775 for safe handling procedures.

Plastic Refractories

Most plastic refractories can be thought of as “firebrick before being fired” since they, like brick, are composed of a highly calcined clay aggregate with a binder of raw plastic clay. The term “plastic” is used because the material is workable, although very stiff, and usually is placed with an air rammer. The air-setting plastics use an aluminum sulfate, an alkali silicate or some other binder to achieve a hard surface before firing, but the primary bond is usually a true ceramic bond that develops at service temperatures above 1800°F.

Phosphate bonded plastics (Type C of Standard Drawing GB-N1268) are an exception; they develop considerable mechanical strength after drying at 230°F and significantly higher strengths after firing at 700°F. The phosphate bonded plastics used in refineries normally have a high alumina composition and show excellent resistance to catalyst erosion.

See Sections 2200 and 2500 for more information on use and installation of plastic refractories. See also IRM-MS-4785 and -4787.

Brick and Special Shapes

Refractory brick, block and special shapes are pre-fired products composed of an aggregate and a binder, often of fire clay. Special shapes are commonly used in furnaces and heaters as burner blocks, floor brick and roof tile. Of the many types of firebrick available, usually only insulating firebrick (IFB), high Al_2O_3 and super-duty fire clay brick are used in refineries and petrochemical plants.

Insulating firebrick (IFB) have been widely used as a lining material for ethylene and primary reformer furnaces. IFB are somewhat similar to (dense) refractory brick made from fire clays, except that IFB are lightweight (35 to 70 lb/ft³), more porous, weaker mechanically and, as the name implies, have better thermal insulating properties. Various classes of IFB are available, with temperature ratings ranging from 2000°F to 3200°F. Air-set mortars are normally used to lay IFB in heaters and furnaces. The mortar used must be chemically compatible with the brick being laid. The brick manufacturer has the mortar recommended for his brick. High Al₂O₃ special shapes are used to form the catalyst support dome in some secondary reformer vessels.

Of the refractory bricks made from fire clays, super-duty bricks are the best and most resistant to high temperatures. They are dense (135 to 150 lb/ft³) and are used in the erection of bridge and divider walls.

See Sections 2300 and 2620 for more information on use and installation of brick and special shapes. See also IRM-MS-4789.

2120 Important Factors in Material Selection

This section opens with a discussion of general things to consider when choosing a refractory material. Sections 2121 through 2128 discuss properties of castables, plastic refractory, and brick. RCF refractory materials are markedly different, and their properties are discussed in Section 2300.

2121 Preliminary Considerations

A number of factors must be considered initially when selecting a refractory material. In a few cases, operating conditions and refractory history are so well defined that very little room for improvement or innovation exists. Even so, a better refractory product for this application may have been just recently developed. This section assesses these preliminary factors.

Erosion Resistance versus Insulating Value

Refractory materials are often selected for use on the basis of either their erosion resistance or insulating value. In general, these are “opposing” properties. A material having good erosion resistance is usually dense, strong, hard and relatively non-porous. It is also a poor insulator. On the other hand, refractories that insulate well have poor erosion resistance, low strength, and are highly porous.

Choosing between these properties is not a problem in most services. For example, because cyclones, which are subject to very erosive conditions, are located inside heated vessels such as regenerators and reactors, cyclone linings do not need to have high insulating value. In other applications where we need good insulating capability and do not need superior erosion resistance, a medium weight insulating material will suffice. Regenerator wall linings are an example where insulating properties are necessary to maintain a low-temperature carbon steel vessel shell.

Physical versus Chemical Properties

For most refinery and petrochemical operations, the physical properties of refractory materials are more important than their chemical properties. However, chemical composition and chemical properties of refractory materials are important in a few applications such as incinerators and secondary reformers.

Available Time for Installation

For new equipment, available refractory installation time generally is not an important consideration. However, time is usually a critical factor during a shutdown (S/D). This is one of the reasons why most vibration cast linings (discussed in Section 2550) are installed in new pipe prior to S/D. During a normal S/D, there just isn't enough time to finish an extensive vibration cast project.

However, sometimes the time required to do a first class job, although longer than the quick fix, does not add to the total S/D time if carefully planned and executed. The amount saved in reduced maintenance costs over time with this approach can be very high. For more information on planning a shutdown, including a suggested time line, see Section 4100, Contracting Plans.

Economic Considerations

When possible, consider the larger picture. For example, it is difficult to justify extensive relining of an obsolete fired heater that is likely to be replaced in a year or so. Another example might be putting a vibration cast lining in a straight section of a flue gas line. Admittedly, the vibration cast lining is the best system, but this could be over-design.

History and Past Experience

How badly is a new type of lining needed? Would another lining system be equally satisfactory or perhaps give longer service? A comment, such as "It looks this bad every time we shut down," should automatically call for an improved refractory design. What is the industry "standard" for this lining application? Are there new developments in lining systems that we should consider? In some cases, the refinery or the operating plant is reluctant to "experiment"—particularly, if the existing lining system has given good service for 10 years or longer.

Operating Conditions

Process conditions must be known for correct materials selection. These conditions include:

- Maximum service temperature
- Maximum gas velocity
- Type of process gas
- Contaminants
- Presence of abrasive particles
- Rapid temperature cycling

2122 Thermal Conductivity and Heat Loss

Thermal conductivity is one of the most important factors in the selection of refractory materials for our applications. Normally, the refractory lining of a vessel (or a fired heater, for that matter) is expected to minimize heat flow from the inside of the vessel to the shell and atmosphere, thereby maintaining the shell temperature within a desired range and saving fuel costs. To design a vessel lining and choose a single-layer (one-shot) castable for the lining, you need fairly accurate thermal conductivity data on the material. Refractory manufacturers usually provide the needed data.

In the case of hydrogen and ammonia plant transfer lines, minimizing heat flow may not be the most important consideration. These lines have historically needed frequent repair due to condensation of gases at the outer shell. Since increasing outer shell temperature (to no more than 400°F to avoid hydrogen attack) can reduce outer shell condensation, and thus the frequency of costly repairs, the cost of heat loss should be weighed against repair and maintenance costs in these lines. See Reference [58] for details on upgrading transfer line design and refractories.

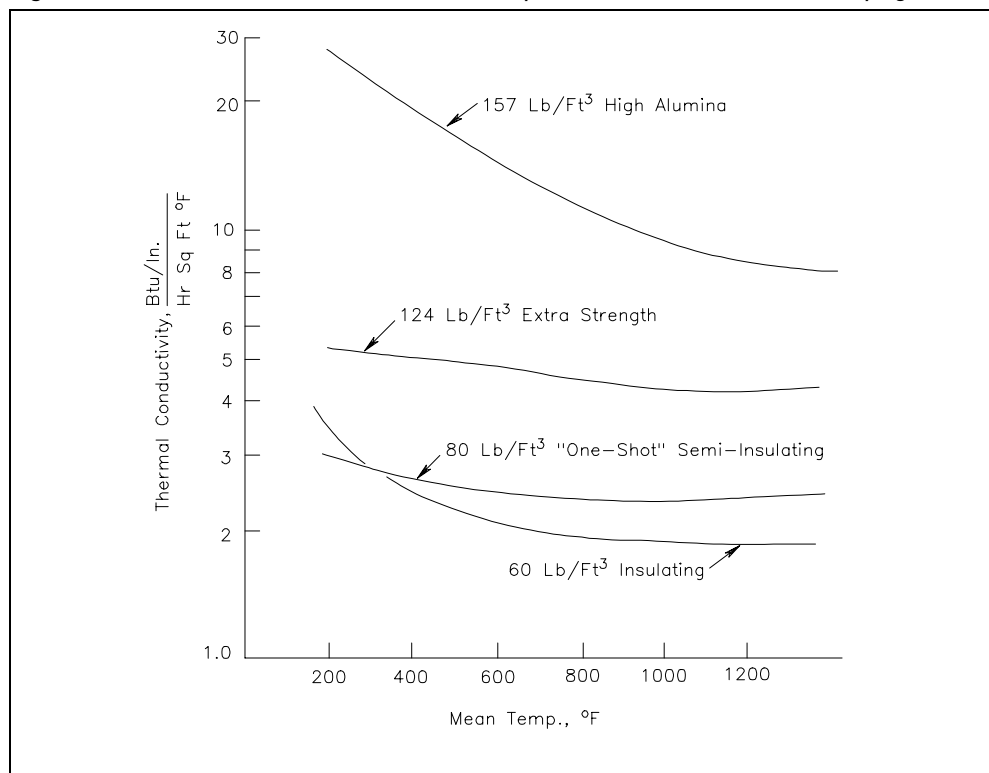
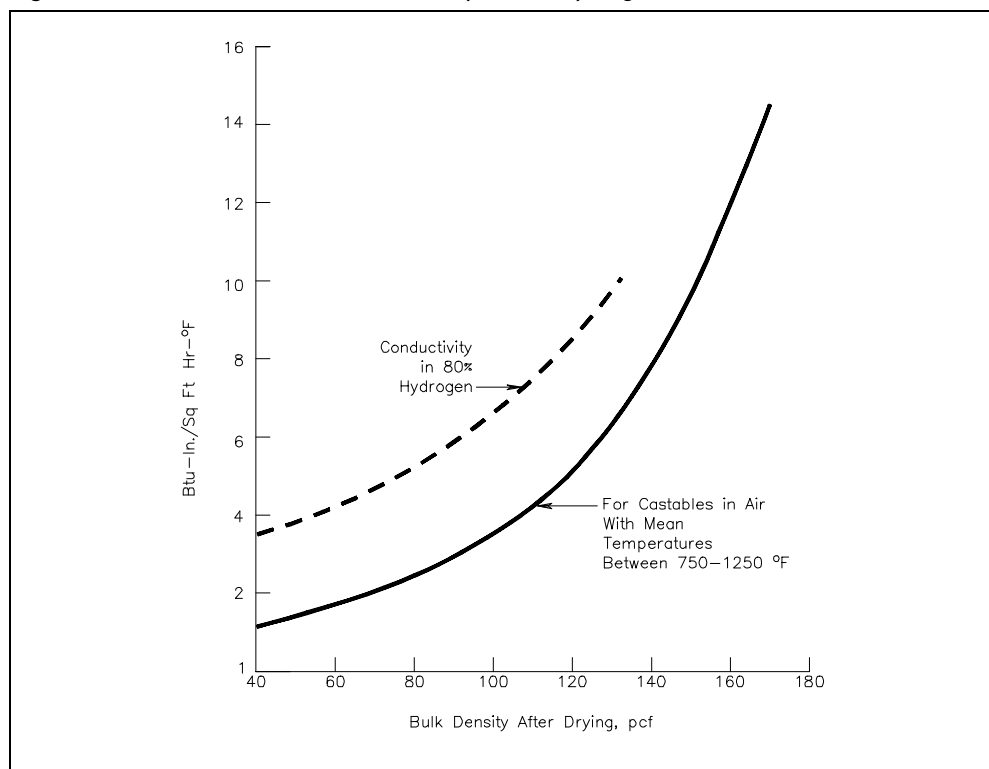
Thermal conductivity (K factor) values in manufacturers' data sheets are not always representative. You will need to know how to use the data and also know their limitations. Keep in mind that the thermal conductivity of a castable is a function of:

- Method of installation
- Mean temperature of the lining
- Thermal history of the lining (to what extent has it been dehydrated?)
- Hydrogen content of the process gas (only a factor in certain cases)

Figure 2100-2 shows the effect of mean temperature on the thermal conductivity of four castables. These castables had been dried at 230°F. As dehydration of the hydrated cement phases continues with increasing temperatures, both density and thermal conductivity decrease. Note that in general the higher the density, the higher the K factor.

Low-cement castables usually have higher thermal conductivity than might be expected from their density. This phenomenon is due to their more highly developed crystalline matrix.

Process Gas and Thermal Conductivity. The effect of high conductivity gases such as hydrogen on the thermal conductivity of castables is shown in Figure 2100-3. The insulating castables with a low-bulk density ($\leq 80 \text{ lb/ft}^3$), and consequently, a high ratio of H_2 -filled pores to solid phase material, show a 200% to 300% increase over the conductivity in air. The denser castables (approximately 120 lb/ft^3) with fewer pores showed only a 50% increase in thermal conductivity when tested in a hydrogen atmosphere. The effects of hydrogen on thermal conductivity must be considered when designing refractory linings for the process gas "side" of ammonia plants and H_2 -producing units. Call Materials Engineering for help if the process stream is more than 25% hydrogen.

Fig. 2100-2 Thermal Conductivities of Refractory Concretes (Castables) after Drying at 230°F**Fig. 2100-3** Curves of Thermal Conductivity in 80% Hydrogen versus Air

Heat Loss Calculations. The following example illustrates thermal calculations used to determine heat flow through a lining and temperatures of the shell and lining. The values of parentheses are example conditions.

The example is for a one-component lining. To calculate heat loss in a two-component lining, add another L/K factor to the denominator of Equation 2100-1.

$$Q = \frac{T_o - T_a}{\frac{1}{h_i} + \frac{L}{K_L} + \frac{t}{K_s} + \frac{1}{h_e}} \quad (\text{Eq. 2100-1})$$

where:

Q = heat loss, Btu/ft² hr

T_o = operating internal temperature, °F
(= 1100)

T_a = ambient temperature, °F (= 80)

h_i = internal film coefficient, Btu/ft² hr °F
(= 40)

h_e = external film coefficient, Btu/ft² hr °F
(= 4)

L = lining thickness, inches (= 4)

K_L = K factor (thermal conductivity) of lining, Btu in/ft² hr °F (= 4.4)

t = shell thickness, inch (= ½)

K_s = K factor for carbon steel shell, Btu in/ft² hr °F (= 300)

Putting numerical values in the equation:

$$Q = \frac{1100 - 80}{\frac{1}{40} + \frac{4}{4.4} + \frac{0.50}{300} + \frac{1}{4}} \quad (\text{Eq. 2100-1})$$

$$Q = 860 \text{ Btu/ft}^2 \text{ hr}$$

Shell temperature and other values may now be calculated as follows.

Outside shell temperature:

$$T_{S''} = T_a + Q \left(\frac{1}{h_e} \right) \quad (\text{Eq. 2100-2})$$

$$T_{S''} = 80 + \frac{860}{4} = 295^{\circ}\text{F}$$

(Eq. 2100-3)

Inside shell temperature:

$$T_{S'} = T_{S''} + Q\left(\frac{t}{K_S}\right)$$

(Eq. 2100-4)

$$T_{S'} = 295 + 860\left(\frac{0.5}{300}\right) = 297^{\circ}\text{F}$$

(Eq. 2100-5)

Hot face of lining:

$$T_{L'} = T_{S'} + Q\left(\frac{L}{K_L}\right)$$

(Eq. 2100-6)

$$T_{L'} = 297 + \frac{(860)(4)}{4.4} = 1079^{\circ}\text{F}$$

(Eq. 2100-7)

Verification of temperature gradient (check on overall calculation):

$$T_O = T_{L'} + Q\left(\frac{1}{h_i}\right)$$

(Eq. 2100-8)

$$T_O = 1079 + \left(\frac{860}{40}\right) = 1100^{\circ}\text{F}$$

(Eq. 2100-9)

Mean shell temperature:

$$T_S = \frac{1}{2}(T_{S''} + T_{S'})$$

(Eq. 2100-10)

$$T_S = \frac{1}{2}(295 + 297) = 296^{\circ}\text{F}$$

(Eq. 2100-11)

Mean lining temperature:

$$T_L = \frac{1}{2}(T_{S'} + T_{L'})$$

(Eq. 2100-12)

$$T_L = \frac{1}{2}(297 + 1079) = 688^\circ\text{F}$$

(Eq. 2100-13)

2123 Erosion Resistance

The resistance of a refractory material to erosion (sometimes erroneously called “abrasion”) is a very important property for a number of applications, especially in FCC units. The erosive medium is finely-divided (150-200 mesh) FCC catalyst which circulates through the unit in large quantities. Erosion has been defined as “the wearing away of material by the cutting action of entrained particles in a high velocity stream.”

The current laboratory test (ASTM C-704) for erosion resistance uses 1000 grams of No. 36 grit silicon carbide to erode a hole in a test sample that is 4½ inches by 4½ inches by 1 inch thick. The weight loss from the test is converted to a volume loss using the plate density which then becomes a direct measure of the size of the eroded hole in cubic centimeters. The ASTM test is an accelerated test (7½ minutes), but results obtained correlate well with service experience.

Erosion Resistance Ratings. The most highly erosion-resistant materials have ASTM C-704 values less than 6 cc. Semi-insulating erosion-resistant materials like those used in catalyst transfer lines will have ASTM C-704 values ≤ 14 cc. Non-erosion-resistant materials used for regenerator wall linings will have ASTM C-704 values of ≥ 100 cc.

For **monolithic-type** refractories, erosion resistance is a function of:

- Porosity of the material
- Type and amount of bond phase (binder)
- Grain size distribution of the aggregate
- Type of aggregate and its hardness
- Compressive strength, but only for materials with strengths ≤ 6000 psi
- Dryout temperature (for many materials). The erosion resistance varies significantly as temperature increases from 230°F to 1400°F

For castables with high compressive strengths (6000 psi to 12,000 psi), there is very little correlation between strength and erosion resistance. Hence, it is very desirable to measure directly the erosion resistance of a castable being installed or being considered.

Erosion resistance requirements for linings in various applications vary widely. The degree of erosion expected in a particular location is a function of:

1. Erosive particle velocity
2. Erosive particle loading in the gas stream
3. Impingement angle
4. Size of the erosive particle

In practice, the size of the particle does not fluctuate widely. Hence, it is common practice to use the most erosive-resistant refractories in cyclones, orifice rings, and catalyst pickup points and to use those with somewhat less erosion resistance in catalyst transfer and flue gas lines. Decreases in porosity due to coke deposition in reactor riser lines have resulted in conventional refractories having much better erosion resistance than expected. In some applications, such as flue gas lines, it is necessary to compromise on a “one-shot” lining having acceptable erosion resistance plus some value as a thermal insulator. For more information on erosion testing, see Reference [58].

Field Abrasion Tester. A portable field abrasion test apparatus is available from some refractory inspection companies. The device works much the same as a standard C-704 machine, but can be run in the field to test as-installed abrasion resistance in any position.

2124 Temperature Limits and Shrinkage

Temperature Limits

Refractory materials have two temperature limits: the temperature at which they begin to shrink (lose volume) and the temperature at which they melt or soften (lose their “refractoriness”). The shrink limit is the lower of the two by several hundred degrees. Manufacturers assign their material a temperature use limit. In most cases the limit they assign equals its shrink limit.

Because of the uncertainty in measuring shrinkage accurately, we recommend specifying a material whose temperature use limit as specified by the manufacturer is approximately 200°F higher than the expected maximum service temperature. This safety factor does not add a great deal to the overall cost of the lining system for most applications.

Most refractory products are rated for temperatures greater than 2200°F. Because most refinery units operate at temperatures of 2200°F and lower, the temperature use limit of the refractory is usually not an important consideration. One notable exception to this generalization is the air preheater in FCC units. In certain types of air preheaters, combustion chamber temperature may exceed 3000°F. Semi-insulating (80 to 90 pcf) castables, used in FCC regenerator linings, are definitely not adequate.

Shrinkage

Castable Linings. Many castables begin to shrink significantly at or near their maximum use temperature. There is even a little shrinkage at 1000 to 1200°F. Some may show excessive vitrification (formation of liquid/glassy phase). Excessive shrinkage of castable linings in service is highly undesirable. Shrinkage causes shrinkage cracks, particularly if metal fiber is absent. These cracks tend to weaken the lining mechanically and may eventually lead to spalling. In some cases, the cracks fill up with catalyst and/or coke, and on cooling, create high stresses in the lining. Acceptable shrinkage values for monolithic refractories, expressed as Permanent Linear Change (PLC) are shown in Figure 2100-5 at the end of this section.

Insulating Firebrick. If not properly fired during manufacture, insulating firebrick will shrink in service or in a laboratory reheat test. An acceptable, high quality IFB will show very little shrinkage when reheat tested at its rated use limit.

RCF Linings. RCF linings are also subject to shrinkage and devitrification of fibers at temperatures near their rated use limit. This is because practically all manufacturers' use limits for RCF products are too high. Devitrification means that very small crystals (generally of mullite) are forming in what was originally an all-glass fiber. Shrinkage of RCF is discussed further in Section 2310.

2125 Strength

Strength is a function of the type and amount of aggregate and cement. Most castables are very brittle, and values for their modulus of rupture (MOR) (flexure) are about 25% of their cold crushing (compression) strength. Their tensile strength is typically only approximately 10% of their compressive strength.

Although high compressive strengths are seldom required in most refinery applications, a high value (greater than 6000 psi) for this property often indicates good erosion resistance. Thermal shock resistance is partly related to strength, and the stronger castables have better shock resistance. Low cement castables are generally less brittle than conventional castables. Thus, they retain more of their strength after exposure to thermal shock.

There is a good correlation between bulk density and cold compressive strength. As a general rule, the dense castables have much better strengths than the insulating castables.

2126 Thermal Expansion

The thermal expansion of some castable materials is theoretically complicated by the expansion of the aggregate and simultaneous shrinkage of the bond phase. This shrinkage (which often occurs in the 350°F to 750°F range) results from dehydration of the binder. The net result is that we do not have to worry about providing expansion joints in refractory concrete linings. Likewise, expansion joints are not required in RCF linings, nor in plastic refractory installations, unless the plastic section connects to firebrick.

Firebrick walls do need thermal expansion joints. A method of calculating their width is given in Section 2320. So-called “expansion joints” in plastic refractory installations are actually contraction joints. They are useful in controlling cracking caused by shrinkage.

2127 Thermal Shock (Spalling) Resistance

Thermal spalling is the fracture or breakage of refractory material resulting from excessive stresses imposed by a sudden temperature change. The stresses develop from unequal rates of expansion and contraction resulting from very rapid heating or cooling. Sudden cooling, e.g., cold water sprayed on hot refractory, is the most common cause. Repeated thermal cycling affects linings the same way that sudden thermal shocks do. It fractures and moves segments of the lining as a result of thermal expansion or contraction.

Laboratory studies of the thermal shock resistance of various materials have shown that:

1. Castables with fused silica aggregate had better resistance to cracking in an H₂O shock cycle than other types of castables.
2. Castables bonded with iron-free calcium aluminate cements were much more shock resistant than those bonded with calcium aluminate cement containing iron.
3. Refractory bricks are much more susceptible to thermal shock damage than are castables or plastic refractory. The difference is thought to be a function of the high degree of vitrification often present in high-fired brick.
4. Refractory bricks with the best resistance to spalling will usually have low thermal expansion rates and high thermal conductivities. These properties minimize the development of temperature gradients within the brick.

2128 Chemical Resistance

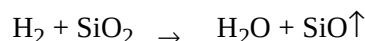
Although the physical properties (erosion resistance, thermal conductivity, etc.) of refractory materials are generally more important than chemical resistance, chemical attack can cause refractory failure in some applications. This attack can be so severe (in a chemical incinerator, for example) that refractory material must be replaced annually.

Incinerators. In the combustion chamber of an incinerator several undesirable ash constituents (e.g., lime, iron oxide, alkali oxides) are present in significant quantities. Some slag attack of the refractory lining is inevitable. A fusion cast refractory lining would undoubtedly resist slagging, but its use would create a serious thermal spalling problem.

Fired Heaters. If significant amounts (2% to 3%) of sulfur are present in the fuel, some types of refractory concretes (particularly the lightweight materials) are subject to sulfuric acid attack from the condensing flue gases.

Certain fuel oils containing both sulfur and vanadium compounds cause a somewhat different problem. Flue gases from the oil burners contain V_2O_5 , which is the prime catalyst for conversion of sulfur dioxide to SO_3 . The latter gas reacts directly with the calcium aluminate binder in the insulating castable lining of the heater. The binder in the castable is partially converted to unstable calcium sulfate, and the lining rapidly deteriorates. Such chemical attack appears to increase with temperature, with the hottest part (approximately 1800°F) of the firebox showing the greatest deterioration. This problem is aggravated by cyclic heating and cooling of the heater. In time, piles of dust and small particles build up on the floor in front of the walls, and the insulating refractory walls become thinner.

Hydrogen and Ammonia Plants. Process gases containing large quantities of hydrogen can attack silica and silicate phases in refractories. The temperature where this attack occurs is generally agreed to be in the range of 1800°F to 2200°F. The free silica or silicates in the refractory react with the hot hydrogen gas to produce gaseous SiO and water:



The extraction of silica weakens the refractory material and may lead to failure. When temperatures decrease downstream in the waste heat boiler, the reaction reverses, precipitating the SiO gas into a fine solid white powder. This phenomenon is especially a concern at the higher-temperature secondary reformer section of ammonia plants. The overall results can be deterioration of the refractory, heat exchange fouling, and possibly catalyst contamination.

Hence, it is very important to use low silica (less than 1.0%) refractories in ammonia plants, or to use fused silica, which is resistant to attack from hydrogen. The Richmond Hydrogen Plant has been successful with Harbison-Walker Lightweight Thermax, with fused silica, in their transfer lines.

In a low-temperature steam environment, carbonic acid and other chemical reactions can condense at the outer shell and attack the calcium aluminate cement in the insulating castable layer. The reports of "mushy refractory," especially at the coldest side of transfer lines, fit this mechanism. Lower calcium aluminate, higher density, higher strength refractory material will resist this attack. Also, designing the outer shell temperature to operate up to about 400°F to reduce condensation will help.

A third mechanism of attack can cause spalling of the refractory. At temperatures over 1300°F, CO combines with iron impurities in the refractory to form iron carbide (FeC). The refractory is crushed as it tries to accommodate the volume expansion when FeC is formed. Therefore, in addition to low silicon, the refractory should be specified as low-iron (<1% Fe) to minimize this problem.

Elevated temperatures and the presence of high pressure steam in the process gases of the reforming section of ammonia plants will destroy the aluminum phosphate bond in phosphate bonded castables and plastics. Such materials should not be used in these applications even for minor repairs and patches.

A 1989 Materials Engineering report [58] is available which recommends methods of transfer line design and refractory choices to reduce repair and maintenance costs in these lines.

Steaming of Refinery Units. Steaming of refinery vessels and lines can seriously weaken the bond phase in phosphate bonded heat-set plastics even when the refractory material has been fired to 800°F. The air-set phosphate bonded castables are much more resistant to steaming. Even these materials will lose strength and integrity if exposed to steaming conditions for long periods of time.

Catalytic Reformers. Operating conditions in naphtha reforming units include hydrogen-rich atmosphere at temperatures of approximately 1000°F. Low-iron castables are used in lining these vessels to protect against catalyst poisoning. Iron, if deposited on the catalyst, reduces its activity. Avoid refractory cements with sulfur content greater than 0.5%.

2129 Thickness Considerations for Refractory Linings

Several calculations and considerations are helpful in determining the optimum thickness of a refractory lining. The most important of these are:

1. Heat loss and shell temperature calculations (Section 2122).

If the process gas contains a significant percentage of hydrogen, it is necessary to increase the K factor of the refractory lining material to compensate for the higher thermal conductivity of H₂ relative to other gases normally present (See Figure 2100-3).

2. Calculation of mechanical and thermal stresses in the lining under operating conditions (Section 2221 and Reference [46]). These calculations are primarily applicable to (cylindrical) vessel linings.
3. Theoretically, erosion resistance must be considered in determining the optimum thickness of a lining. In practice, however, erosion is not a problem in many lining applications. When erosion resistance is an important consideration, the design approach is to specify (and install) refractory materials that will not erode significantly. In the case of thin erosion-resistant linings (e.g., cyclones), we recommend one-inch thick linings rather than ¾ inch. This is largely a function of economics—the “extra” 33% of lining thickness doesn't cost very much.

Figure 2100-4 shows which of these considerations are important for specific applications.

Fig. 2100-4 Economic Thickness Considerations for Refractory Linings

Equipment/ Lining	Heat Loss & Shell Temp.	Mechanical/ Thermal Stress	Erosion Resistance	Hydrogen Effects	Comments
FCCU Regenerator	Y	Y	N	N	
FCCU Reactor	Y	Y	N	N	
FCCU U-bends, Y-sections, other external cold wall T.L.	Y	N	Y	N	The erosion resistance of lining in reactor riser lines 'improves' with service by coking.
FCCU Regenerator Cyclones	N	N	Y	N	
FCCU Reactor Cyclones	N	N	Y	N	Linings must be resistant to startup steaming
FCCU Flue Gas Line	Y	Y	Y	N	Erosion resistance is particularly important at ells.
FCCU Steam Generators	Y	N	Y med	N	Some linings could be subject to mechanical/ thermal stresses
FCCU Slide Valves	Y some parts	N	Y	N	May be either hot wall or cold wall design
FCCU Seal Pots	N	See Comment	Y some		Thermal shock resistance is very important
FCCU CO Boiler	Y	N	Y med	N	Refractory requirements vary with design.
Naptha Reformers Reactor Wall	Y	Y	N	Y	Use shroud and vapor stop rings to minimize gas by-passing
Hydrogen and Ammonia Plants: Transfer lines and waste-heat boilers	Y	Y	(1)	Y	Space limitations often 'control' thickness & type of lining
Hydrogen & NH ₃ Plants Primary Reformer	Y	N	N	N	Lining varies with design and supplier
NH ₃ Plants Secondary Reformer	Y	Y	N	Y	Design of lining is a function of whether or not the shell is H ₂ O-cooled.
Sulfur Plants Reaction Furnace	Y	N	N	N	Hot face lining is preferably ~90% Al ₂ O ₃ brick. Allow for longitudinal expansion.
Ethylene Furnaces	Y	N	N	N	Lining varies with design and supplier. Some brick usually involved.

(1) In some plants, erosion may not be a consideration, and a one-component lining may be successful. Contact the Materials Unit for advice.

2130 Additives

We normally consider only two types of additives for monolithic refractories: metal fibers and organic fibers.

2131 Metal Fiber Reinforcement

The use of stainless steel needles in monolithic refractories, particularly castables, goes back to the early 1970's. About 1975, this technology advanced with the introduction of the melt-extraction process. This process gives a fiber with a kidney bean-shaped cross-section and an approximate diameter of 0.020 inches. These melt-extracted needles are softer than cold-drawn wire, and refractories with metal fiber additives can be easily gun-applied. Cold-drawn wire has the drawback of being stiffer than melt-extracted needles and tends to plug the hose of pneumatic gunning equipment.

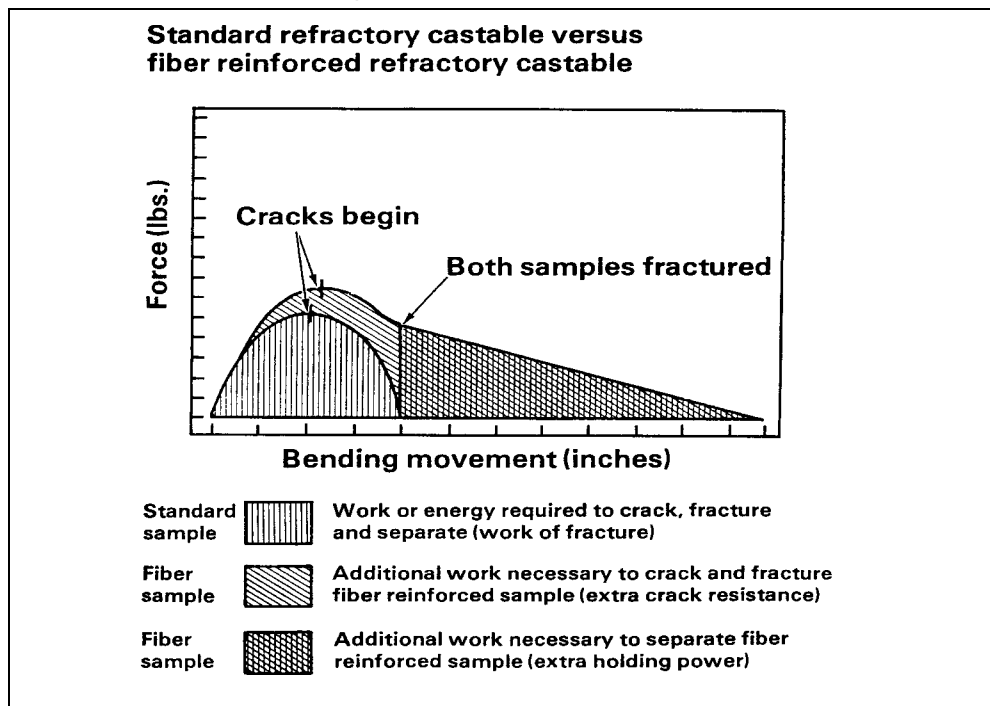
Advantages. The advantages of stainless steel needles in monolithic linings are numerous. In order of importance, they are:

1. Cracked and spalled fragments of the lining are held in place by the interlocking nature of the fiber matrix. After identical modulus of rupture (MOR) testing of two bars of refractory material, one with needles and the other without needles, the bar containing needles is not broken even though a crack is present. [41]
2. The additional work necessary to separate fiber reinforced material is high. [8] See Figure 2100-5.
3. Anchorage requirements are reduced. For example, use of needles lets us design workable and satisfactory monolithic lining systems with individual anchors rather than hexmesh.
4. The refractory lining has better thermal shock and impact resistance.
5. The crack pattern in the lining that occurs after drying and firing is different and improved. The cracks are not as wide in linings with needles even though they may be more numerous.
6. The needles impart some flexibility to the lining.

Limitations. Service temperature is the major limitation to the use of stainless steel needles. Some deterioration of the fiber matrix at the hot face can be tolerated if the needles in the cooler portion of the lining remain effective. Since linings are usually heated from only one side, advantage may be taken of the thermal gradient through the lining. If most of the lining is below 2000°F, the addition of stainless steel needles is probably warranted.

Needle Metallurgy. Needles are available in a wide variety of alloys. Type 304 stainless steel can be used for most refinery applications since operating temperatures are generally $\leq 1400^{\circ}\text{F}$. For service at higher temperatures, consider Type 310 or 330 needles. Consider the type of atmosphere that the needles will be exposed to, particularly if any corrosive elements are present.

Fig. 2100-5 Typical Work of Fracture *From a paper delivered at the Refinery and Petrochemical Plant Maintenance Conference, 1981 [8] by M. S. Crowley. Information courtesy of Harbison Walker Refractories.*



2132 Organic Fiber (Rapid Fire Additive)

Refractory manufacturers have promoted another additive, very small diameter (0.0005 inch) organic fiber, as a means of eliminating explosive (steam) spalling in castables. This type of additive (some varieties are proprietary) is always added by the manufacturer of the castable during the primary blending operation.

Theoretically, the small fibers burn out of the castable during dryout (or initial heating) and leave a network of fine pores which help water and steam escape from the lining. Hence, explosive spalling is much less apt to occur.

Where Used. Although their merit is sometimes questioned, use of organic fiber in refractories reduces risk of explosive spalling while not reducing erosion resistance, insulation value or strength very much. Their use does not result in inferior properties and the fibers are relatively inexpensive to add.

This additive should be considered for use with thick linings of high-density castables where curing temperatures will be below 70°F.

Limitations. There are two minor drawbacks to the organic fiber:

1. Fibers reduce strength of the castable by a small amount (about 5%).
2. Fibers have been known to separate from the castable material in the package, but this has not proven to be a recurring problem.

2140 Typical Failure Mechanisms

Design and materials engineers, maintenance supervisors, and installation inspectors all need to know what causes refractory linings to fail. In some cases, changes in start-up and/or operation procedures will help solve a refractory problem, but these kinds of solutions are infrequent. Most of the time we need better design, materials, and/or improved installation.

Before discussing individual failure mechanisms, one other general comment is appropriate. During the past 40 years or so, many so-called “refractory failures” were really failures of the anchors and/or the anchorage system, including hexmesh. Fortunately, the development and use of metal fiber reinforcement has alleviated anchorage problems to some extent. Nevertheless, the importance of anchorage in refining/petrochemical refractory linings cannot be over-emphasized.

2141 Thermal Shock and Spalling

Failures in gun-applied vessel linings are most often due to spalling, i.e., peeling-off of large thin slices of lining. This is really not thermal spalling although spraying cold water on hot refractory in the early stages of a turnaround may hasten the failure. The usual causes of this spalling are listed below in order of their importance.

Poor Installation Techniques. Laminations in the lining due to poor gunning practices and to not “squaring off” the lining when interruptions occur are frequent causes of spalling. Overwatering of the refractory while gunning, which results in wider shrinkage cracks, is a secondary cause.

Overthickness. A too-thick lining causes excessive compressive stress and mechanical spalling in the hot face of the lining. Underthickness and/or external insulation can also cause problems, but these are unlikely to occur.

Mechanical Strains caused by pipes, beams and manway openings going through the lining.

Water on Hot Surfaces. Thermal shock and thermal spalling do occur in flue gas lines when defective or failing spray-nozzles allow water to impinge directly on hot (approximately 1250°F) refractory. Seal pots are another place where thermal spalling is a problem. Refractory linings in seal pots can change from soaking wet to about 1300°F in a few minutes. The reverse change (dry to wet) also takes place in a few minutes.

2142 Erosion

Most cyclone lining failures are the result of erosion over extended time periods. Occasionally a thin layer of refractory will pop out of a hexagonal enclosure. This is a form of spalling and is probably a result of heating and cooling of hexmesh-encased lining material. Close inspection of the cyclones during shutdowns will show important differences in the refractory wear patterns. Analysis of these

differences can determine the cause of wear: catalyst impingement, plastic refractory lamination (pop-outs) or other causes of failure.

Lining failures from catalyst erosion also occur in Y-sections, catalyst transfer lines, and flue gas ducts. In most cases, failure does not imply complete loss of the lining, but rather, erosive wear to the point that something must be done (either repair or partial replacement). In flue gas ducts, erosion is more of a problem at elbows than in straight runs. It is particularly severe in and just downstream of restriction orifices and slide valves.

2143 Bypassing of Hot Gases

Factors that cause bypassing to become a problem generally involve pressure differential (e.g., the ΔP across a catalyst bed, shroud and/or vapor stop cone). In all cases, the effect of bypassing is a hot spot on the shell. Some examples follow.

1. In catalytic reformers, the major failure problem is hot spots on the shell caused by process gas flowing between the lining and the shell. Any failure of the shroud-to-head weld (at the top of the vessel) will result in an immediate hot spot at the weld junction.
2. Certain designs of crossover lines in ammonia plants use shrouds and vapor stop cones with insulating castable refractory as a lining system. A weld failure, particularly at the junction of the cone and the shell, will cause a hot spot.
3. Catalyst and hot gas bypassing at the grid seal was a probable factor in at least one FCCU regenerator failure. Two things were wrong: the grid seal was improperly installed and the anchors did not hold the one-shot lining tightly against the shell. Anchors having greater holding power are available now and should be used in vessel linings.
4. A two-component lining system, consisting of 3 inches of erosion-resistant castable backed up by 2 inches of insulating castable, was pneumatically installed in part of a flue gas line in 1975. Anchorage for this lining was independent two-component anchors on 8-inch centers in a square pattern. The lining performed satisfactorily for several years. Eventually, cracks and laminations in the erosion-resistant (hot face) layer permitted flue gas and catalyst to reach the softer insulating castable. In time, this backup layer was partly eroded and hot spots occurred. Metal fiber was not used in the hot face layer.

2144 Differential Thermal Expansion

There have been many partial failures of two-component linings involving, typically, a 3-inch thick insulating back-up layer and a 1-inch thick erosion-resistant castable hot face layer in hexmesh. This lining system includes stud bolts welded to the shell, square coupons attached to the stud bolts, and, finally, hexmesh carefully welded to the coupons. The cause of most of these failures is the difference in the average thermal expansion coefficient of Type 304 stainless steel hexmesh and the other components in the lining system. In other words, when the FCCU is heated up

and put “on stream,” mechanical stress present in the hexmesh tends to break the welds at the weakest points in the system.

This instability is aggravated by heating and cooling the lining system and possibly by coke buildup within and behind the hexmesh layer. In the reactor riser line, it is not uncommon to see black, coke-filled refractory and hexmesh that has broken loose from the coupons and grown in area. This growth is a cyclic process resulting from the filling of small cracks and pores in the erosion-resistant castable with hard coke each time that the unit goes on stream (after a shutdown). Coke impregnation prevents the hexmesh from returning to its original location against the shell when it is cooled to ambient temperature. With repeated cycles, additional coke deposits build up, eventually causing the hex-to-shell welds to be overstressed and fail.

2145 Failure of Exterior “Linings”

Some FCCU regenerators have air distribution rings in the bottom of the regenerator. Some FCCUs have risers and standpipes that pass through part of the regenerator. Other large diameter piping is often present inside the larger regenerators. It is sometimes desirable to install anchorage and a refractory “lining” on the outside of these pipes, either to minimize thermal stresses on certain welds or prevent erosion. The lining may consist of a semi-insulating castable or a phosphate bonded castable. Such linings should contain metal fiber reinforcement and are generally 1 inch or 2 inches thick, but some have been as much as 4 inches thick. In rare cases, an annular space was provided between the outside of the pipe and the inside surface of the lining.

The failure mechanism for an exterior lining is usually related to thermal expansion coefficients. The piping which usually is filled with hot air or hot gases is often Type 304 stainless steel. This metal has a much greater expansion coefficient than the lining. Hence, the pipe expands more than the lining when the unit is put “on stream.” This puts the lining in tension (particularly when an annular space for pipe expansion is not provided) and causes it to crack. This cracking eventually develops to the point where mechanical spalling occurs. The extent of the failure after two or three runs is a function of how well the lining system was designed and installed initially. A thin layer of 1/8-inch ceramic fiber blanket can be used to provide an expansion cushion for the pipe. This is frequently used on nozzle penetrations.

2146 Loss of Anchorage

Other than the aforementioned failure of hexmesh anchorage, loss of anchorage, per se, is unusual at this time. We still hear of failures related to insufficient anchors and problems with too many anchors (in some repair situations), but widespread failure of independent anchors in a lining system is very rare. Better anchors are available now and our understanding of anchors and anchorage systems is vastly improved. Wavy Vee and double hook anchors have superior holding power. Footed anchors make attachment welding easier to perform. Anchor spacing, pattern and orientation must be carefully specified and inspected.

2147 Mechanical Impact

Impact damage to refractory linings is more apt to occur during initial installation or during a shutdown than when the unit is operating.

2148 Chemical Reactions

A few examples of refractory failure mechanism involving chemical reactions follow.

1. Some hydrogen units use steam reforming to generate large quantities of CO. At temperatures of 800°F to 1200°F, atmosphere containing $\geq 30\%$ carbon monoxide will react with iron-containing refractories and cause layers of carbon deposits around each iron site. This process results in carbon monoxide disintegration of the refractory.
2. Many years ago, a test installation of phosphate bonded plastic refractory in hexmesh was “washed out” of some Y-sections in an FCCU by start-up steaming. Since the refractory had not been baked at 700°F minimum, the result is not surprising.
3. Catalyst support domes in certain secondary reformer vessels were formed with 90% Al_2O_3 fired shapes. This vessel is part of the gas reformer section of an ammonia plant. After 23 months' service, the bottom surface of one such dome showed a significant reduction in SiO_2 content (from approximately 8% to 3%). This result was associated with a shallow (structural) spalling or blistering. The spalled pieces were about 3/16 inch thick and quite friable. X-ray diffraction analyses showed that mullite present in the original refractory had been destroyed. Large percentages of both steam and hydrogen are present in the process gas that passes through openings in the catalyst support dome. In all probability, high-pressure steam was the major factor in SiO_2 removal. The exposed surfaces of the dome continued to deteriorate and it was replaced after about 7 years of service.

2150 Factors in Developing a Recommended Brands List

2151 Refractory Material Requirements

Chevron has developed nine classifications of refractory materials to help field engineers with refractory selection. The Company has defined each classification by specifying its physical properties. The classifications, called Types A through I, are defined on Standard Drawing GB-N1268.

This drawing has several uses. (1) The engineer can use it to specify (by type) the refractory material to be used for a job. (2) The requirements of each classification can be used as pass-fail criteria for prequalification and production testing. Manufacturers' data sheets often report typical or average values. These values are useless when testing a batch of material for acceptance. (3) Standard Drawing GB-N1268

gives specific criteria for evaluating a material for inclusion on the Recommended Brands List.

2152 Recommended Brands List

The Company has developed a Recommended Brands List (Form IRM-EF-881) of refractory materials. This list is in the Standard Drawings and Forms section of Part 2. Products are on the list if they:

- Meet the physical requirements of their type (A through I of Standard Drawing GB-N1268)
- Have a proven record of experience
- Are of comparable cost

The manufacturers on the Recommended Brands List were selected on the basis of (1) their proximity to Chevron installations, (2) their range of products, (3) the quality of their technical help, and (4) their commitment to product development.

1. All manufacturers on the list are major suppliers of refractory materials to the petroleum/ petrochemical industry. They have manufacturing plants near major Chevron installations, which minimizes our shipping costs. The cost of surface transportation can exceed \$100 per ton throughout the continental U.S. Air freight costs for refractory material are much higher than surface shipping costs. For example, the cost per pound to Hawaii in 1988 ranged from \$.50 to \$1.00, equal to \$2000 per ton.
2. To be on the list, manufacturers must have a wide range of products available. (Most manufacturers supply eight of the nine classes.) This requirement eases the burden of prequalification testing at more than one plant.
3. Manufacturers must also have qualified technical representatives available to help solve material selection or field installation problems.
4. Development of new refractory products is important. Manufacturers must have research/development staffs who continue to improve products.

For addresses of manufacturers, see Section 4100, Contracting Plans.