A Chapter in the *Refractories Handbook*, edited by
Charles A. Schacht, and to be published by Marcel Dekker, Inc.,
New York, NY 10016

Alumina-Silica Brick

by

Denis A. Brosnan, Ph.D, PE
Clemson University, Clemson, SC 29634-0971

Introduction

With the advent of the Iron Age, people began learning in earnest how to construct furnaces that could withstand sustained temperatures exceeding the melting point of iron (1535°C). At the melting point of iron, magnetite (Fe_3O_4) can be reduced to iron at an oxygen partial pressure of about 10^{-7} atmospheres – an atmosphere easily reached in a furnace packed with a form of carbon such as coke or charcoal. Of course, carbon-saturated iron has a melting point of 1152°C, but the iron must be at a higher temperature to attain sufficient fluidity for casting.

With the advent of a larger demand for iron objects in commerce, modern ferrous metallurgy was born. It cannot be overemphasized that the iron and steel industries, with ever-increasing demands for better refractory products to combat more severe service conditions, drove innovations with alumina-silica brick over history. All other industries consuming alumina-silica brick, including non-ferrous metals and minerals processing, benefited from this progression of technology.

Alumina-silica brick have the attributes of being relatively inexpensive – at least compared to most basic brick. In addition, alumina-silica brick can be used in situations where modern castable refractories have disadvantages. While some castable products have achieved physical properties meeting or exceeding those of brick, there is still a responsibility with castable for correct installation, curing, and preheating. If time or local skills for installation are constraints, brick may be a preferred solution. In some types of furnaces, the use of bricks may be preferred to avoid mechanical or thermal shock damage that reduces furnace life. Finally, tradition with use of bricks still influences some product decisions in applications like ceramic kilns, incinerators, and smaller boilers.

The technology of alumina-silica brick is relatively uncomplicated. In other words, the phase relationships and properties listed in specifications are straightforward. With more in-depth study, the researcher finds that natural raw materials and their inherent variability always influence the average properties and variance in properties in the refractory brick as-manufactured. In addition, no two refractory plants are ever exactly the same meaning that processing equipment influences the quality of the end product. Finally, alumina-silica brick are manufactured on a tonnage scale meaning that the products exhibit variability in properties attributable to this scale of manufacture. All of this contributes to the correct observation that one product in the same “class” can be better than a competitive product of the same class. The differences between the “good” and “not-as-good” products are usually not revealed in physical property tests alone. Further testing or experience are required to understand the fine points of why one product may be better than another one.

A Brief Historical Perspective

The earliest refractories used in furnaces were natural stones quarried into brick-like shapes and natural clays and sands used as rammed lining components. Brick-like shapes were used because of the thousands of years of practice using stone and clay masonry in buildings. So it was natural that bricks would be used as furnace linings became larger than simple enclosures.

People found that some natural stones and some clay had better thermal resistance than others. In particular, some stones or clays exhibited better “refractoriness” than others. A simple definition of refractoriness is that the material will not melt or deform (shrink) under prolonged service in the furnace environment in service. Excessive shrinkage almost always results in opening of joints in a furnace, cracking, increased susceptibility to thermal shock, and a host of other problems.

It became fairly obvious that chemical analysis of the natural material was linked to its refractoriness just because lighter colors, for example, indicated less iron content and generally greater refractoriness. Certain clay became known as “fireclay” because of its resistance to high temperature. Clays in certain regions of various countries became preferred for use in refractory products based on their reputation as successful raw materials for refractories.

In time, conveniently located natural stone products were depleted. This resulted in production of hand molded fireclay bricks. With the onset of the industrial age, fabrication of bricks in mechanical presses began. Sufficient temperature could be reached in downdraft kilns to produce qualities of refractory brick in the late 1800’s not too unlike those available today.

With the advent of phase equilibrium diagrams after about 1920, the modern era of alumina-silica brick began. At that point, scientific principles guided the development of fireclay brick rather than trial and error with different sources of raw materials. World War II was particularly influential in the history of alumina-silica bricks as it marked the development of refractories in North America based on bauxite as an alternative to the basic refractories that were suddenly unavailable from Europe. The development of the Bayer process for manufacturing aluminum brought about the manufacture of calcined and tabular alumina – generating a new line of “high alumina” brick. Processing technology in grinding, separation, mixing, pressing, and firing increased dramatically after World War II giving “modern” plants a technology edge over older facilities.

Developments with refractory concrete or “castable” eventually caused alumina-silica brick consumption to peak and begin a decline starting in the late 1970’s and the early 1980’s. Technical improvements in all types of refractory products caused a reduction in refractory consumption rates. The end result has been a decline in production of alumina-silica refractories. In today’s global economy, alumina-silica brick are primarily produced in emerging countries and exported to “developed” countries. While the production and consumption patterns have shifted, there remains a need for understanding of the technology in today’s world.

The Technology of Alumina-Silica Refractories

Phase Relationships in The System Al_2O_3 -SiO_2

The technology of alumina-silica refractories is traditionally explained using the alumina (Al_2O_3) – silica (SiO_2) phase equilibrium diagram (Figure 1). A phase diagram is essentially a “map” of temperature versus composition showing “phases” or discrete areas/volume elements of similar composition within a material at equilibrium at a given temperature. The idea is that certain compositions will produce certain qualities of refractories. The diagram in Figure 1 shows composition in mole percent and temperature in degrees Celsius. There are updated representations of this system, but the essential facts remain the same.

The *essential facts* from this phase diagram are:

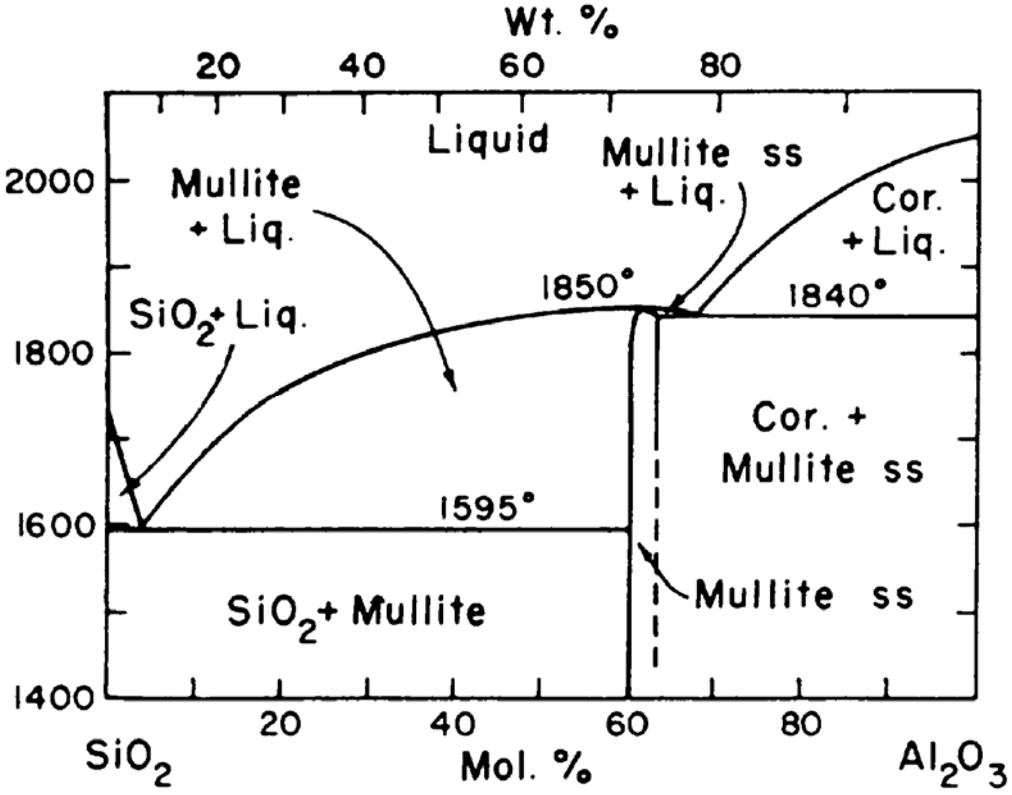
- One compound known as *mullite* ($3Al_3O_3 \cdot 2SiO_2$) is formed as a reaction product or consequence of heating mixtures of alumina and silica. The theoretical composition of mullite is 71.6% Al_2O_3 and 28.4% SiO_2 on a weight basis (or 60 mole percent Al_2O_3). Mullite is a very refractory compound exhibiting a melting point of $1850^{o}C$. As the mullite content of a refractory increases as the composition approaches 72% Al_2O_3, the refractoriness of the material usually increases due to the presence of the mullite. Near the theoretical composition of mullite, a mullite solid solution (denoted “*mullite ss*”) forms.

- The diagram has a “*solidus*” line at $1595^{o}C$ meaning that compositions ranging from just below 100% SiO_2 (>0% Al_2O_3) to the mullite composition (60 mole % Al_2O_3 or ~72 weight% Al_2O_3) exhibit solid phases (for example cristobalite – a form of SiO_2 - or glass and mullite) unless the temperature exceeds $1595^{o}C$ (the binary eutectic temperature between SiO_2 and mullite). The term “glass” signifies the presence of a vitreous and non-crystalline phase. It can be present along with a small percentage of “free” or uncombined crystalline silica. Above $1595^{o}C$, a refractory in this composition range would be obviously useless as it would be only liquid phase or melted (denoted as "*Liq*." In Figure 1).

- Above about 72% Al_2O_3, the solidus line is located at 1840°C indicating compositions in the range of just above 72% Al_2O_3 to just below 100% Al_2O_3 exhibit no melting until 1840°C is exceeded. As the composition approaches 100% Al_2O_3, *the refractoriness of the material usually increases. Pure* Al_2O_3 *(*corundum – labeled as "*Cor*." In Figure 1) has a meting point of about 2050°C.

Figure 1: The Alumina-Silica Phase Equilibrium Diagram

(Arakami and Roy,1962)



The Al_2O_3 - SiO_2 phase diagram can be used to explain the general "classes" of alumina silica brick in terms of generalized "refractoriness". These classes are given in Table 1 along with general comments on use of the products. It is easy to see that as you progress across the chart to the right (increase the Al_2O_3 content of the refractory), the refractoriness *increases* either because the mullite content increases and/or because the solidus temperature jumps up above 60 mole % Al_2O_3. The refractoriness increases because the glass content (quantity of vitrified phase) decreases leading the material to have higher resistance to shrinkage on prolonged high temperature exposure.

There are natural “lines of demarcation” on the chart. Since refractory fireclays typically contain a maximum of 38-40% Al_2O_3, the refractories made solely from clay are in the fireclay class and have use limits approaching 1600^oC (Table 1). Minerals with the next highest alumina content include sillimanite, kyanite, and andalusite – all containing about 60% Al_2O_3. Therefore, brick in the 50% and 60% Al_2O_3 classes must substantially contain these latter minerals giving them higher use temperatures. The next mineral substance containing higher alumina used in refractories is calcined (burned) bauxite that forms a basis for 80% and 85% Al_2O_3 class products. For higher alumina content, synthetic or Bayer process calcined and sintered (tabular) alumina must be used. Tabular alumina aggregates and calcined alumina are used in products in either the 90% or 99% Al_2O_3 classes of refractory brick.

Any discussion of alumina-silica refractories must include the effects of “fluxing” oxides in the raw materials as they affect properties of the refractory. In natural clays, alkali is present in various forms – with the alkali content expressed as sodium oxide (Na_2O) or potassium oxide (K_2O). Both of these are powerful fluxes influential in the firing of fireclay brick and influential with respect to their performance in service. Other fluxes such as calcium oxide (CaO), iron oxide (FeO or Fe_2O_3), and titanium dioxide (TiO_2) are present. More flux generally means more glass will be present in the fired refractory. It is for this reason that fireclay brick, in particular, may exhibit better service performance (for example, greater spalling resistance) if they contain lower levels of flux; i.e. greater mullite content increases spalling resistance and greater glass content decreases spalling resistance.

As a final note on phase equilibria, refractories are usually not at thermochemical equilibrium. This means non-equilibrium phases may be present. An example might be a fireclay brick containing calcined bauxite aggregate (as a contaminant) with an overall composition of 50% Al_2O_3. This fired brick will contain corumdum even though the phase diagram says it should not be present. Given an unusually long time during the firing process, the corundum would disappear (forming mullite). Phase diagrams always indicate the *direction* for potential reactions in refractories, but they do not provide assurance that the reactions will go to completion.

Table 1: Classes of Alumina-Silica Brick Explained In Terms of the Al_2O_3 –SiO_2 Phase Equilibrium Diagram

Al_2O_3 Range in Most Standards	**Common Terminology** ***Phases***	**General Performance** ***In The Absence of Slag Corrosion or Alkali Attack Conditions***
Less Than 50% Al_2O_3	Fireclay (Chamotte) *Phases on Phase Diagram: Mullite and Glass (Can Contain “free SiO_2 ”).*	• Usually made from 100% fireclay. • Highest quality grades usable to about 1600°C (“superduty” brick). • Typically contain 38-42% Al_2O_3 and are based on fireclay minerals.
50% Al_2O_3 or 60% Al_2O_3	Sillimanite, Andalusite, or Kyanite *Phases on Phase Diagram: Major Phase - Mullite and Minor Phase - Glass (Can Contain “free SiO_2”).*	• Cannot be made from 100% clay since clays do not contain sufficient Al_2O_3. • Made from 60% alumina minerals and contain some fireclay. Can be made with bauxite and clay. • Can be used to in excess of 1700°C .
70% Al_2O_3	Mullite *Phases on Phase Diagram: Major Phase – Mullite. Products made with bauxite contain corundum, mullite, and glass.*	• Made either from “bauxitic clay” or calcined bauxite and clay. • Can be used in excess of 1750°C.
80% Al_2O_3 and 85% Al_2O_3	Bauxite *Phases on Phase Diagram: The major phase is corundum with a minor quantity of mullite and glass.*	• Made from calcined bauxite. • Usually used in aluminum contact refractories.
90% Al_2O_3	Alumina *Phases on Phase Diagram: The major phase is corundum with a substantially minor quantity of mullite and glass. Brick for molten iron contact usually contain fused Al_2O_3 for enhanced abrasion resistance.*	• Made from tabular and/or fused synthetic (Bayer process) alumina aggregates. • Can be used in excess of 1800°C.

Refractory Raw Materials

Raw materials for use in alumina-silica brick are available throughout the world in discrete deposits found useful in refractories. The typical chemical analyses for materials used as “major mix constituents” are given along with calcination temperature in Table 2. Calcination, if employed, renders the material as volume stable to resist shrinkage up to the original calcination temperature. Many other raw materials are used in manufacturing refractories serving distinct purposes. For example, in brick manufacture “bond clay” is used to promote cohesion in the pressed mass so the brick can be lifted off of the press for subsequent drying and firing. Bond clay is typically an aluminous clay exhibiting plasticity when wet. An excellent review of raw materials used in refractories is available by Nishikawa.

Refractory producers may have a unique or “standard” compliment of raw materials in their inventory to produce all of their alumina-silica brick products. Any one producer may have a special material that is unavailable to other producers. In North America, this was the case for Missouri diaspore until its depletion in the 1960’s. As another example, one refractory producer had special bauxitic kaolin in Alabama used to produce 70% Al_2O_3 brick, and the deposit was subsequently depleted in the 1980’s. In both cases cited, the producer with the special raw material had a competitive advantage during the life of their particular mineral deposit.

Table 2: Typical Raw Materials Used in Alumina-Silica Brick

Information	**Fireclay (Calcined Basis)**	**Andalusite**	**Calcined Refractory Bauxite (Guyana)**	**Tabular Alumina**
Usual Calcination Temperature, ^oC	Can be used as calcined aggregate (1450^{o}C+) or as raw clay.	Not calcined	1450^{o}C	>1750^{o}C
Chemical Analysis, %				
Al_2O_3	39.7	61.3	88.7	99.5
SiO_2	54.0	37.4	6.5	<0.1
TiO2	2.80	0.25	2.84	Tr.
Fe_2O_3	1.90	0.48	1.43	0.05
MgO	0.30	0.13	0.31	0.05
CaO	0.20	0.20	0.15	0.07
Na_2O	0.20	0.08	Tr.	0.25
K_2O	0.60	0.06	Tr.	Tr.
LOI	0.15	0.13	0.05	0.04

Special Changes in Raw Materials on Heating

Fireclay

The chemical and physical changes in clay materials on heating and cooling are reported in a number of classic references (See *Grimshaw*). These changes are summarized, in brief, as:

- *Dehydroxylation* of clay minerals in the range of 400-600°C involving decomposition of clay crystals with consequent release of water vapor.

- *Inversions* and *conversions* of "free" silica (SiO_2) phases that involve potentially destructive volume changes. The well-known alpha to beta quartz inversion is seen at 573°C.

- *Partial fusion* and *permanent shrinkage* at temperatures approaching "red heat" (above 950°C).

The dehydroxylation of clay can be represented by the non-reversible chemical reaction for kaolinite (the major mineral in fireclay):

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O = Al_2O_3 \cdot 2SiO_2 + 2H_2O$$

or

kaolin decomposes to "*metakaolin*" plus water vapor

It is well known that, on additional heating, the metakaolin forms mullite at about 1020°C. In doing this, excess silica is released in a sequence of steps by metakaolin with the end result being mullite dispersed in a vitreous (glassy) phase.

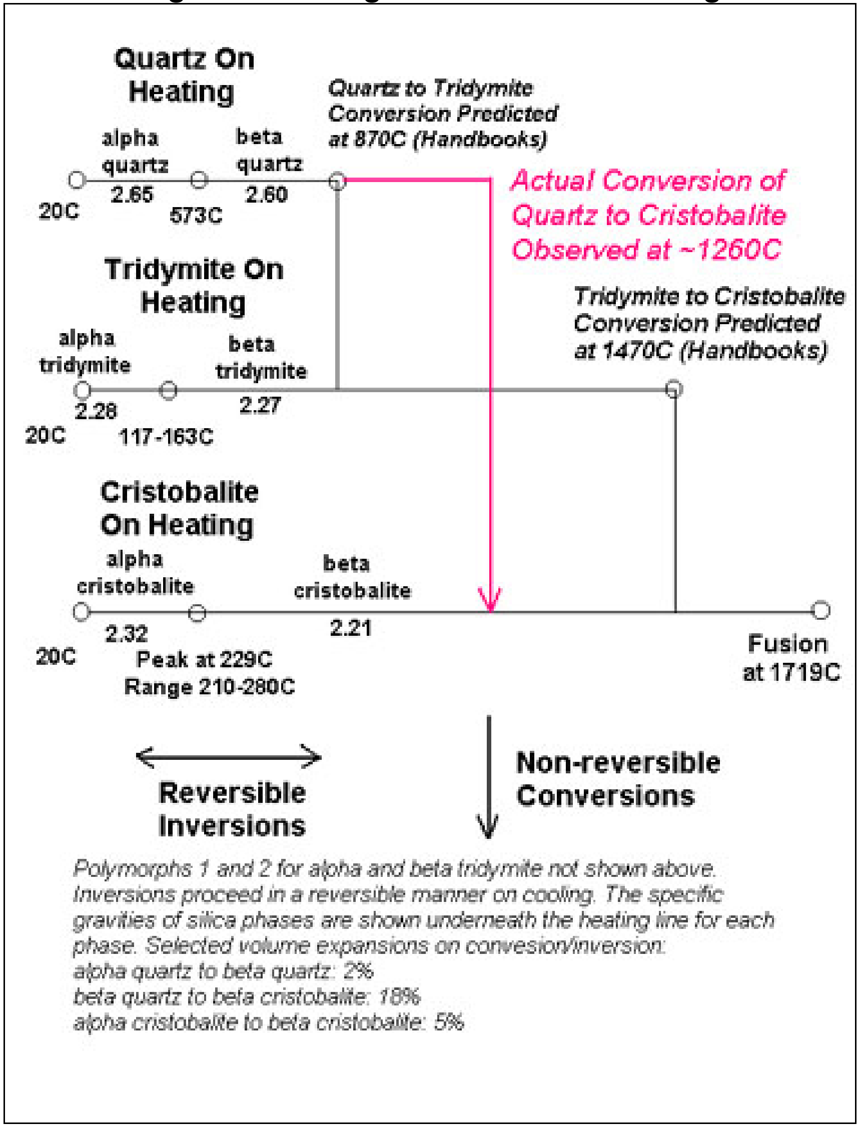
It is also well known that fireclay contains a small amount of "free" or *uncombined* silica – usually as quartz in the mineral deposit. However, quartz is not the only mineral of pure silicon dioxide (SiO_2). The other silica minerals are *trydimite* and *cristobalite*. In fact, quartz can be "converted" into either tridymite and/or cristobalite on heating.

The form of quartz in the earth is called alpha (α) quartz. It is also called "low quartz" because it occurs at ambient temperatures in natural minerals. On heating of α-quartz, a new form called beta (β) quartz is formed at 573°C at one atmosphere of pressure. The process is called an "inversion" because it involves a slight change in separation of silicon and oxygen atoms while maintaining the same spatial arrangement or crystal structure. This inversion is reversible, i.e. it occurs on heating or cooling if free quartz is present.

The densities of α-quartz and β-quartz are 2.65g/cm^3 and 2.60g/cm^3 respectively. This means a lower density quartz form is created on heating forcing a volume increase to take place. The volume change on inversion of α-quartz to β-quartz is small, just two percent, implying a linear expansion of about 0.7%.

On further heating, quartz is *converted* to either tridymite or cristobalite in a non-reversible transformation. The complete transformation scheme for silica (SiO_2) is given in Figure 2. Inversions are illustrated by a circle on a horizontal line representing one of the three forms of silica (quartz, tridymite, and cristobalite). The inversions only involve a slight change in atomic separations, and an inversion is reversible. “Conversions” are changes involving formation of an entirely new mineral with a new crystal structure, and vertical arrows illustrate the conversions. The densities of all silica forms are given on the diagram.

Figure 2: Changes in Silica on Heating



Polymorphs 1 and 2 for alpha and beta tridymite not shown above. Inversions proceed in a reversible manner on cooling. The specific gravities of silica phases are shown underneath the heating line for each phase. Selected volume expansions on convesion/inversion:
alpha quartz to beta quartz: 2%
beta quartz to beta cristobalite: 18%
alpha cristobalite to beta cristobalite: 5%

The actual conversions of silica are influenced by the impurities in clay meaning that the actual conversion temperatures are different than those published in textbooks for pure silica. For example, fireclay brick can contain cristobalite if they are fired above about 2250°F (1230°C). The transformation from β-quartz to β-cristobalite causes a total permanent volume expansion of 13%. This is counterbalanced in fireclay brick manufacture by shrinkage during vitrification.

The problem with free cristobalite in fireclay refractories is that it causes deterioration in refractories on continued reheating and cooling in a process called "dunting". Dunting results in cracking and eventual fragmentation of refractories that contain too much cristobalite. The cause is the volume expansion during inversion of α-cristobalite to β-cristobalite on heating of 5% (or shrinkage on cooling). It is well known that dunting can occur well after the refractory has cooled in a process called "delayed dunting".

Recrystallization of Sillimanite Minerals and Bauxite on Heating

The sillimanite family members, used to produce 50% and 60% alumina class brick, all exhibit characteristic permanent expansions on heating due to decomposition of the mineral and the formation of mullite. This is usually of interest in alumina-silica brick on heating the brick for the first time (during manufacture). The decomposition temperatures and expansions are given in Table 3.

Table 3: Changes on Heating of Sillimanite Family Minerals

Mineral	Decomposition Temperature, °C	Volume Expansion, %
Sillimanite	1530-1625	5.6
Andalusite	1350-1500	4.9
Kyanite	1325-1410	18.8

If the brick is fired below the decomposition temperature of the mineral and used above the decomposition temperature of the mineral, the expansion will be realized in service. This could be detrimental to the refractory if there is inadequate expansion allowance in the lining. In certain cases, limited "after expansion" is important to obtaining good refractory life – as in rotary kiln applications.

There is a different situation with calcined refractory grade bauxite. The original calcination temperature is approximately 1450°C, and this is a normal peak firing (sintering) temperature for bauxite based refractory brick. If these brick are used above the original calcination and firing temperature, further "recrystallization" takes place resulting in significant expansions. For example, the permanent linear expansion on exposing these products to temperatures reaching 1600°C is in the range 2-4%. The actual mechanism contributing to the expansion is likely additional mullite formation and growth of corundum crystals within the bauxite aggregates.

Alumina-Silica Brick Manufacturing

Alumina-silica brick are manufactured from a blend of sized raw material aggregates and clays by mixing, forming, drying, and firing. These are traditional processes in manufacturing any ceramic product. Since refractories are used at elevated temperatures, they are particularly sensitive to contamination. Segregation of particle sizes also leads to low bulk density in brick products.

Throughout history, many fireclay brick have been made by the extrusion process or by extrusion followed by “repressing”. Extrusion always means higher water contents must be used in processing to obtain plasticity meaning that the product will have higher apparent porosity than dry pressed product. Modern super duty fireclay and high alumina brick are made by dry pressing. Dry pressing has the attribute of producing generally finer pore sizes and structures in the fired product as compared to extruded products. This impacts fracture toughness and thermal shock behavior of the brick.

The best alumina-silica brick are made in plants with common attributes. If an inspection trip is made to a refractory plant, here are the attributes worth looking for:

- Raw Material Storage – Storage should free of opportunities for contamination by inadvertent mixing of lower quality raw materials with higher quality raw materials.

- Particle Sizing and Sized Material Storage – How many aggregate storage bins are observed for a particular raw material? A modern dry pressed brick should contain at least four size fractions of the major raw material – coarse, medium, fine, superfine, etc.

- Mixing – Is a modern high intensity mixer used in production? Muller mixers (with large wheels) were obsolete in the 1970’s.

- Conveyance –Are conveyors covered to prevent contamination? If bucket elevators are used, is the manufacturer trying to prevent particle size segregation?

- Presses – Are the presses computer controlled and do they automatically compensate for thickness variance in pressed brick?

- Kilns – Are the kilns computer controlled? Do they have modern high-velocity burner systems?

The most modern high alumina brick plant is designed to minimize contamination and particle size segregation. This ultimately results in a smaller variance in physical properties in products made in such plants as compared to products from older or dirtier plants.

Properties and Microstructure of High Alumina Brick

Fireclay Brick

Fireclay brick are classed in standards based on their refractoriness or ability to withstand high temperatures without shrinking and spalling. In North America, the classes were “low heat duty”, “medium heat duty”, “high heat duty”, and “super duty”. The general composition and typical properties are given in Table 4. One measure of refractoriness is Permanent Linear Change (PLC) – the permanent shrinkage (or expansion) on heating to a specified temperature for a specified time with no load applied. Many people refer to PLC as “Reheat Expansion” or “Reheat Shrinkage”.

Table 4: Typical Composition and Properties of Fireclay Brick

	Low Duty 1000°C Max.	**Medium Duty 1200°C Max.**	**High Duty 1400°C Max.**	**Superduty 1600°C Max.**
Chemical Analysis				
Al_2O_3	25.4	29.3	37.0	41.9
SiO_2	68.1	62.9	57.8	53.2
Fe_2O_3	1.5	2.3	1.3	1.0
TiO_2	1.5	2.9	2.3	2.2
Na_2O+K_2O	1.5	1.5	1.3	1.2
Physical Properties				
Bulk Density, g/cm^3	2.00	2.10	2.11	2.35
Apparent Porosity, %	19.0	20.5	18.0	12.5
Modulus of Rupture, MPa	5.2	3.8	9.7	8.5
Crushing Strength, MPa	28	32	35	22
PLC, 5 hr. @ 1400°C			-0.2 to +0.2	
PLC, 5 hr. @ 1600°C				0.0 to –1.2
Load Test, 172 kPa and 1.5 hr.			0.5 to 1.5 @ 1350°C	1.5 to 3.0 @ 1450°C

A typical fireclay refractory brick will exhibit reversible thermal expansion of 3/32” (2.38mm) per foot (305 mm) of length on heating from room temperature to 2400^{o}F (1315^{o}C). This is equivalent to a thermal expansion coefficient of 6.0exp(-6)/^{o}C, i.e. 6.0X10^{-6} mm/mm/^{o}C or 3.35exp(-6)/^{o}F, i.e. 3.35X10^{-6} in/in/^{o}F.

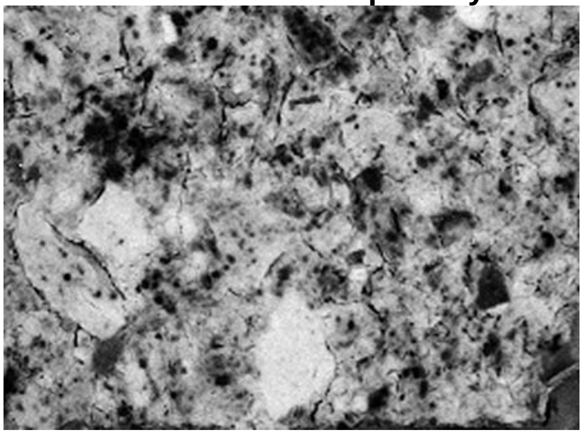
Most brick manufacturers recommend an “expansion allowance” (expansion joint allowance) equivalent to 3/32” for fireclay brick linings for each foot of lining length (horizontal traverse). This prevents undue loading and damage to the fireclay bricks in the wall due to superimposed stress if the lining is constrained from movement when heated.

Permanent expansion or shrinkage usually affects the hot face region of the refractory (hot side). In linings where movement is expected – as in rotary kilns – consideration must be given to the combined potential for reversible thermal expansion and for permanent expansions or shrinkage.

There is usually not a clear-cut link between composition and properties for fireclay brick products. This is because a multitude of factors determine the “refractoriness” of the clay used in the manufacture of fireclay bricks. Like most ceramic products, certain strength properties usually improve as bulk density improves. However, as density improves, spalling resistance may decline. It is best to look for combinations of properties that contribute to success – like density and PLC together.

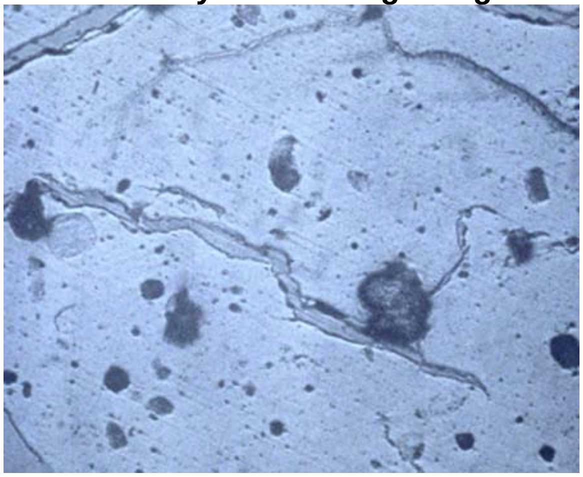
The microstructure of a fireclay brick is shown in Figure 3 at very low magnification in reflected light. This brick was fabricated by dry pressing of calcined aggregates and a raw clay blend. Considerable shrinkage of the “matrix” around coarse aggregate particles has created obvious cracks around the aggregate particles.

Figure 3: Microstructure of A Superduty Fireclay Brick



At higher magnification, the nature of pores in a typical fireclay brick can be seen (Figure 4). The elongated nature of most pores in the calcined aggregate particle is seen along with rounded pores. The continuum of mullite and glass cannot be seen at this magnification. Etching techniques and higher magnification must be used to reveal the mullite crystals.

Figure 4: Fireclay Brick at High Magnification



130X

Fireclay brick are susceptible to alkali attack, and the usual route for alkali to enter the refractories is through vapor phase permeation of the refractory brick through the hot face. Two consequences are possible: (1) fluxing of the surface ("glazing") and (2) formation of new phases resulting in expansion of the refractory.

Glazing of the surface of the refractory and within the refractory immediately behind the hot face is possible given sufficient surface temperature of at least 1125°C and given accumulation of sufficient alkali. The lowest melting liquid phases that form compounds expected when alkali contacts fireclay are given in Table 5. Even lower melting liquids may exist as non-equilibrium or transient phases.

Table 5: Alkali Phases Formed At The Hot Face Of Alumina Silica Brick Resulting in Localized Melting

Alkali	Phase Expected	Melting Point of Phase, °C
Na_2O	Albite $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	1118
Na_2O	Carnegite $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$	1399
K_2O	Sanidinite $K_2O \cdot Al_2O_3 \cdot 6SiO_2$	1510
K_2O	Leucite $K_2O \cdot Al_2O_3 \cdot 4SiO_2$	1693

The expansion of fireclay brick is observed in alkali rich atmospheres and at temperatures at or below where glazing is expected or where there is prolonged alkali exposure with low concentration of alkali in a furnace atmosphere. It is well-known that a new phase called kaliophilite ($K_2O \cdot Al_2O_3 \cdot 2SiO_2$) will form in fireclay refractories exposed to potash (K_2O) vapor. This causes a localized volume expansion of about 15% that can result in cracking and “disintegration” within the refractory. Potash vapor is particularly expected in combustion atmospheres where wood is the primary fuel and where glazing of ceramic ware is practiced. Alkali resistance tests can be found in standards for refractories.

Fireclay brick are also subject to carbon monoxide “disintegration” due to their iron oxide content. The mechanism is formation of iron carbide (Fe_3C) when the fireclay brick is exposed to carbon monoxide (CO) gas in the temperature range of about 400-800^{o}C. The formation of iron carbide causes “destruction” of the refractory structure. Carbon monoxide disintegration tests are found in refractory standards. Reactions usually given for this process are:

$$3Fe_2O_3 + 9CO \rightarrow 6Fe + 9CO_2$$

And subsequently

$$3Fe + 2CO \rightarrow Fe_3C + CO_2$$

Spalling or thermal shock damage of fireclay refractories has always been a concern of furnace designers and operators. It is not always obvious which brand of fireclay brick will exhibit the best spalling resistance from physical property data alone. Three different brands of fireclay brick are given with their physical properties and spalling loss in laboratory tests in Table 6.

It is apparent from Table 6 that chemical analysis and PLC alone do not correlate with spalling behavior. However, alkali content apparently affects both subsidence under load and it provides improved spalling resistance. This shows that even apparent minor differences in alkali content are important in the performance of fireclay brick. The alkali content of the brick influences the glass content of the brick, and higher glass contents are detrimental to spalling resistance.

Table 6: Spalling Behavior of Three Fireclay Brick Brands

	Conventional	**High Density**	**Premium**
Chemical Analysis			
Al_2O_3	50.8	53.2	52.9
Alkalis	1.5	1.2	1.2
Physical Properties			
Bulk density, g/cm^3	2.18	2.34	2.34
PLC, 5 hrs. @ 1480^oC	0 to -0.6	0 to –1.2	-0.3 to – 1
Subsidence under load %, 5 hrs. @ 1450^oC, 172kPa	-3 to –5	-1.5 to -3	-1.5 to –2.5
Subsidence under load %, 100 hrs. @ 1450^oC, 172kPa	-10 to –14	-6 to –10	-2 to -6
Panel spalling Loss, %, 1650^oC Preheat	3 to 8	2 to 6	0 to 3

Semi-Cordierite Brick and Kiln Furniture

Kiln furniture, setter block for kiln cars, and ceramic components are frequently manufactured in a composition close to that of a synthetic mineral named cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2$). Pure cordierite contains 13.7% MgO, and it exhibits a low thermal expansion coefficient of 3exp(-6)/^oC. Because of its low thermal expansion coefficient, cordierite materials usually have excellent thermal shock characteristics.

Pure cordierite is an expensive material, and it is known that less pure materials containing some cordierite also exhibit low thermal expansion coefficients. For this reason, “semi-cordierite” materials are frequently used as kiln furniture and car deck block in ceramic kilns. In some cases, alumina-silica brick compositions are also used for the same product applications. Properties of some products used in kiln furniture/deck block applications are shown in Table 7. The maximum use temperature of these products is typically 1200^oC or higher.

The relationship between MgO content and thermal expansion coefficient is seen in Table 7. At very low MgO content, the thermal expansion coefficient approaches that of fireclay brick or mullite [~6exp(-6)/°C]. The microstructures of typical products of this type are shown in Figures 5 and 6.

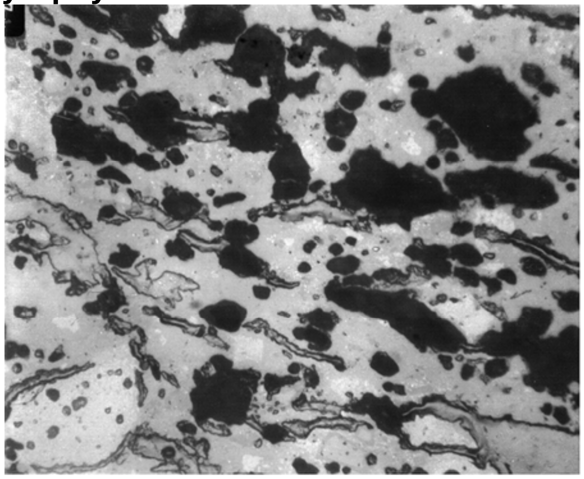
Table 7: Composition and properties of Kiln furniture/Deck Block Products

	Semi-Cordierite Pyrophyllite Aggregate (Extruded)	**Semi-Cordierite Pyrophyllite Aggregate High Fired (Extruded)**	**Semi-Cordierite Clay Aggregate (Pressed)**	**Semi-Cordierite Clay Aggregate (Pressed)**
Chemical Analysis				
Al_2O_3	36.2	33.3	32.0	37.7
SiO_2	57.4	61.8	59.1	45.7
Fe2O3	1.6	1.3	2.9	1.7
MgO	3.0	2.0	0.9	12.8
Physical Properties				
Bulk density, g/cm^3	2.13	2.12	2.13	2.04
Apparent porosity, %	18	20	19	23
Compressive Strength, MPa	41.4	20.7	38.5	53.8
Subsidence under load, %, 100hrs.,172kPa, 1315^{o}C	-2.0	-1.0	NA	NA
Coefficient of Thermal Expansion	3.3exp(-6)/^{o}C	3.1exp(-6)/^{o}C	5.9exp(-6)/^{o}C	2.8exp(-6)/^{o}C

NA = Not available.

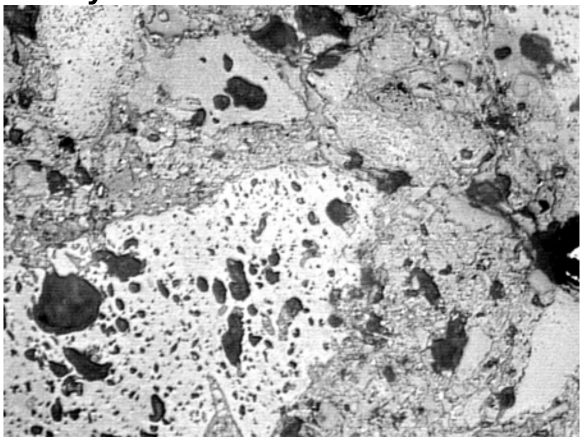
The microstructure of the extruded semi-cordierite material exhibits “slit-shaped” pores as are typical of extruded clay products (Figure 5). It is not obvious from this photomicrograph that the size of the pyrophyllite aggregate particles is large – in some cases approaching 3-4 mm. By contrast, the microstructure of the pressed semi-cordierite material exhibits fireclay aggregate particles surrounded by a matrix of sintered clay with pores that are primarily rounded (Figure 6). Many authorities attribute improved thermal shock resistance to the presence of fine rounded pores. For that reason, it is possible that the pressed product containing ~0.9% MgO (Table 7) might exhibit similar performance with the extruded product containing 3.0% MgO.

Figure 5: Microstructure of Extruded Pyrophyllite Based Semi-Cordierite Brick



100X

Figure 6: Microstructure of Pressed Clay Based Semi-Cordierite Brick



100X

A typical contaminant in semi-cordierite brick is cristobalite formed as “free” silica as quartz in the raw materials is converted to cristobalite when the refractory is fired to temperatures of at least 1300°C. By reference to an MgO-Al_2O_3-SiO_2 phase equilibrium diagram (not shown), one can see that free cristobalite is an equilibrium phase unless the composition of the product is exactly that of pure cordierite. Excessive cristobalite content can cause “dunting” and reduced life of kiln furniture/block. Cristobalite can be conveniently determined using X-ray diffraction or thermal analysis techniques.

Insulating Firebrick

Insulating firebrick (IFB) were developed in the 1930's, and they were the predominant form of insulation until the development of insulating castable and fiber refractories. There are two types of brick: (1) brick based on clay and gypsum using the burn out of sawdust to create high porosity (and thereby provide better insulating value) and (2) brick based on lightweight aggregate and clays. Like all alumina-silica brick, insulating firebrick have a duty rating (service limit). This duty rating is commonly used in the product names – as in K-20 for a 2000°F (1093°C) duty limit. Some data on IFB's is given in Table 8.

Table 8: Composition and Properties of Selected Insulating Firebrick

	K-20	**K-23**	**K-26**	**JM-30**
Use Limit	2000°F (1093°C)	2300°F (1260°C)	2600°F (1427°C)	3000°F (1649°C)
Chemical Analysis				
Al_2O_3	39	39	58	73.4
SiO_2	44	44	39.1	25.1
Fe_2O_3	0.4	0.4	0.7	0.5
CaO	16	16	0.1	-
Alkalis	0.4	0.4	1.7	0.9
Physical Properties				
Bulk density, g/cm^3	0.48	0.50	0.85	1.01
PLC, %, @ Indicated Temperature (1066°C) and after 24 hr.	0 @ 1066°C	0 @ 1232°C.	-0.2 @ 1400°C	-0.6 @ 1620°C
Subsidence under load, % @ Indicated Temperature, 1.5 hr., 69kPa	0 @1066°C	- 0.2 @ 1204°C	-0.2 @ 1204°C	-0.1 @ 1204°C
Thermal Expansion Coefficient/°C	5.4exp(-6)	5.4exp(-6)	NA	NA

It is important to note that the permanent linear change data is based on a 24-hour test exposing the brick to the test temperature. For long-term exposures near the rated service temperature, shrinkage may occur sufficiently to allow joint opening. For this reason, it can be important to use IFB's with a higher duty rating than seems required by the process temperature alone.

Insulating firebrick are susceptible to alkali attack. The products made using gypsum and sawdust burnout material (indicated by high CaO contents) may undergo an expansion reaction in a service environment containing alkali. In some cases this reaction has been deleterious and reduced service life. By contrast, the IFB made with lightweight aggregate may experience surface glazing in an alkali environment.

Insulating firebrick remain a choice for construction and repair when castable or fiber products may not be preferred. IFB's constitute the working lining of many furnace structures. Construction is usually convenient since most IFB's can be cut with a hacksaw. Caution should be used in selecting IFB's when abrasion resistance or impact resistance is required.

50 and 60% Alumina Class Brick

Refractory brick in the 50 and 60% Al_2O_3 classes exhibit improved refractoriness over fireclay products. There are two fundamental mineral mixtures used in producing these classes of brick, and the physical properties of the products depend, in part, on which mineral mixture was used in the manufacture.

The most straightforward way to produce brick in this class is to use 50% Al_2O_3 or 60% alumina aggregates (i.e. bauxitic kaolin or andalusite). Another way to produce these classes of product is to use a mixture of bauxite and fireclay. This latter method has been termed the "bauxite dilution" method. In other words, bauxite (at 88% Al_2O_3) is diluted with calcined fireclay and raw clay (at ~40% Al_2O_3) to produce the required alumina content. Properties of these types of refractories are given in Table 9.

It is important to state that refractories containing bauxite or andalusite typically exhibit high reheat expansion while clay brick do not. In refractories containing andalusite and also containing clay, this tendency for high reheat expansion may not be observed. Thus, there is a fundamental difference in the bricks within the same class with respect to permanent expansion characteristics. In linings requiring the extreme tightness – as in rotary kiln applications – the reheat expansion may be extremely important in good lining life.

By contrast, high reheat expansion may be associated with high spalling tendency, i.e. low spalling resistance. In this regard, brick produced from bauxitic kaolin, i.e. "clay base", may have superior spalling resistance. This is because of their finer texture, i.e. smaller average pore size and due to the absence of permanent expansion reactions on heating.

The TiO_2 content of bricks may indicate the fact that they contain calcined bauxite aggregate (if ≥2.5%). Bauxite can also be recognized on a broken or saw cut surface as a gray appearing aggregate to the naked eye.

Table 9: Composition and Properties of 50 and 60% Al_2O_3 Class Brick

	50% Al_2O_3 Clay Base	**50% Al_2O_3 Bauxite Base**	**60% Al_2O_3 Clay Base**	**60% Al_2O_3 Bauxite Base**	**60% Al_2O_3 Andalusite Base**
Chemical Analysis					
Al_2O_3	50.5	49.5	58.1	62.1	58
SiO_2	44.5	49.5	38.2	32.5	39
Fe_2O_3	1.3	1.3	1.2	1.2	1.5
TiO_2	2.3	2.5	2.2	2.6	0.2
Alkalis	0.8	0.7	0.1	0.8	≤0.3
Physical Properties					
Bulk Density, g/cm^3	2.38 to 2.45	2.37	2.52	2.50-2.59	2.55
Apparent Porosity, %	11 to 16	17.5	14.3	17-20	≤15
Modulus of Rupture, MPa	13.8-20.7	7.6-12.4	18.2	10.3-15.2	
Crushing Strength, MPa	48-69	28-55	58	34.5-62	≥60
PLC, 5hrs. @ 1600°C	+0.5 to +1.5	-1.0 to + 1.0	-0.1	+2 to +4	
Panel Spalling Loss, %, 1650°C Preheat	<5	3-8	<2	3-5	

70% Alumina Brick

After World War II, 70% Al_2O_3 Class refractories became a “workhorse” in industrial furnaces because of their high use or duty ratings and because of their durability in many processes where slag corrosion or other reactions take place. This class of refractories can either be produced from bauxitic clays exhibiting 70% Al_2O_3 or by using appropriate mixtures of bauxite (88% Al_2O_3) and fireclay (~40% Al_2O_3). As in the case of 60% Al_2O_3 brick, the mineral base of the firebrick makes a profound difference in physical properties and thermal response of 70% Al_2O_3 class brick.

The chemical composition and physical properties of the two types of 70% alumina brick are given in Table 10. The brick based on calcined bauxite exhibits much higher reheat expansion (PLC) and higher spalling loss than the brick based on bauxitic clay. On the other hand, the brick based on calcined bauxite may have superior performance where erosion resistance is required.

Table 10: Composition and Properties of 70% Al_2O_3 Class Brick

	Bauxitic Clay Base	**Calcined Bauxite/Clay Mix**
Chemical Analysis		
Al_2O_3	71.8	70.1
SiO_2	22.9	23.6
Fe_2O_3	2.3	2.0
TiO_2	0.2	3.0
Alkalis	0.3	0.3
Physical Properties		
Bulk Density, g/cm^3	2.51	2.60
Apparent Porosity, %	21.0	20.0
Modulus of Rupture, MPa	9.3	9.7
Crushing Strength, MPa	57.6	38-65
PLC, 5hrs. @ 1600°C	+0.9	+2-+4
Panel Spalling Loss, %, 1650°C Preheat	0	≤15

The microstructures of the two types of 70% Al_2O_3 brick are shown in Figures 7 and 8. In Figure 7, the brick is made from calcined aggregates, which exist, surrounded by a finely textured matrix. The distribution of medium size particles around coarse aggregates is excellent. This microstructure suggests excellent spalling resistance.

By contrast, the brick made from calcined bauxite has a completely different appearance. The dark bauxite particles predominate the microstructure, but a calcined clay aggregate particle is evident in the lower right of the photomicrograph of Figure 8. A glassy matrix containing mullite surrounds all particles A comparison of Figures 7 and 8 provides graphic evidence that brick in the same alumina class can have completely different composition, and the microstructures alone suggest that key reheat (PLC) properties of these brick will be different.

Figure 7: 70% Al_2O_3 Brick Based on Bauxitic Kaolin

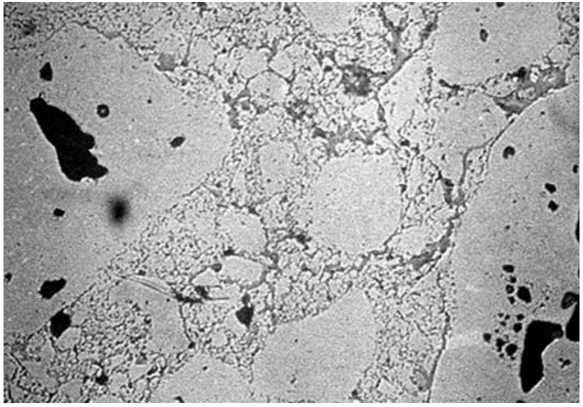
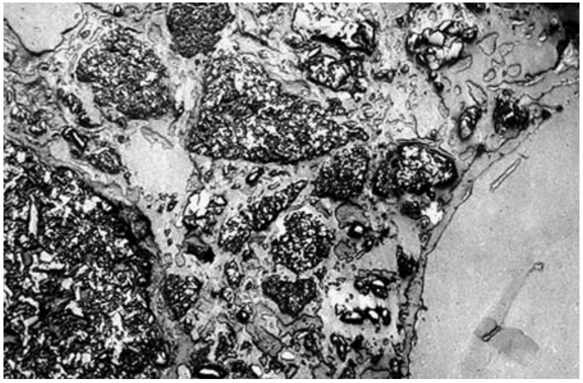


Figure 8: 70% Al_2O_3 Brick Based on Calcined Bauxite and Clay



80 and 85% Alumina Brick

Brick in the 80 and 85% Al_2O_3 class were originally developed for use in aluminum melting and holding furnaces. It is rare that they find application in other types of furnaces. These brick are based on calcined bauxite, as it is the closest mineral in alumina content to their overall composition.

The properties of 80 and 85% Al_2O_3 brick are given in Table 11. The resistance to aluminum attack is, in part, due to the resistance of the bauxite to solution in molten aluminum and to salt fluxes that may cover the metal bath. Generally speaking, these brick have not been successful in ferrous foundry or incinerator applications. The reason may be the relatively poor refractoriness of the bond phase (glass and mullite) holding together very refractory calcined bauxite aggregate. In an aggressive slagging situation, the bauxite aggregate is eroded out of the brick, and wear rates are usually unacceptably high.

Table 11: Composition and Properties of 80 and 85% Al_2O_3 Class Brick

	80% Al_2O_3	**85% Al2O3**
Chemical Analysis		
Al_2O_3	79.9	84.1
SiO_2	13.6	7.3
Fe_2O_3	1.2	1.1
TiO_2	3.6	2.6
Alkalis	0.6	0.2
Physical Properties		
Bulk Density, g/cm^3	2.72-2.82	2.82-2.92
Apparent Porosity, %	15-18	14-17
Modulus of Rupture, MPa	11-17	27
Crushing Strength, MPa	48-69	83-110
PLC, 5hrs. @ 1600°C	+0.5 to +1.5	-0.5 to+0.5
Panel Spalling Loss, %, 1650°C Preheat	0-5	0-5

90 and 99% Alumina Class Brick

Brick in the 90 and 90% alumina classes are among the highest strength and erosion resistant of refractory bricks. They are made from synthetic (Bayer Process) alumina aggregates, and some types may contain fused alumina for special erosion resistance. It is not surprising that there are several distinct types of brick in the 90% Al_2O_3 class.

The composition and properties of bricks in the 90% Al_2O_3 class are given in Table 12. The type denoted “Fused Alumina – Mullite Matrix” is a product designed in the 1950’s for channel induction furnaces for iron foundries. The fused alumina provides very high erosion resistance to flowing molten iron. The microstructure of this type is shown in Figure 9 where fused alumina aggregate particles (white with rounded black pores) are surrounded by a gray matrix containing a lighter mullite phase. Rounded pores are seen in Figure 9 with surface detail created by polishing media on resin impregnant (used for polishing purposes).

The type denoted as “Tabular Alumina – Corundum Matrix” is made from coarse super-calcined alumina aggregates and reactive calcined alumina fines to produce a “direct bonded” microstructure where alumina-to-alumina bonding (corundum to corundum) predominates. This provides an obvious increase in hot modulus of rupture (Table 12). The microstructure of this type of brick is shown in Figure 10. In the lower field, a tabular alumina aggregate particle resides, and it is connected to the matrix through bonds with smaller corundum crystals.

Table 12: Composition and Properties of 90% Al_2O_3 Class Brick

	Fused Alumina *Mullite Matrix*	**Tabular Alumina *Corundum Matrix***	**Alumina Chrome**	**Alumina Chrome *Spall Resistant***
Chemical Analysis				
Al_2O_3	91.4	90.1	89.7	83.0
SiO_2	8.1	9.5	0.5	2.0
Fe_2O_3	0.3	0.1	0.2	0.1
Cr_2O_3	0.0	0.0	9.0	11.2
TiO_2	Trace	Trace	0.1	Trace
Alkalis	0.2	0.2	0.1	0.2
Physical Properties				
Bulk Density, g/cm^3	2.72-2.82	2.98	3.17	3.20
Apparent Porosity, %	15-18	16	17.8	17.5
Modulus of Rupture, MPa	11.7-17.2	16.1	31	11
Modulus of Rupture @ 1482^oC, MPa	≤5.2	9.1	13	10
Crushing Strength, MPa	48.2-68.9	78.2	86	84
PLC %, 5hrs. @ 1705^oC	0 to +1.5	-0.2		
PLC %, 5hrs. @ 1816^oC			+0.7	-0.1
Panel Spalling Loss, %, 1650^oC Preheat	0-5	0-2	0-2	0

Figure 9: 90% Al_2O_3 Brick Based on Fused Alumina Mullite Matrix

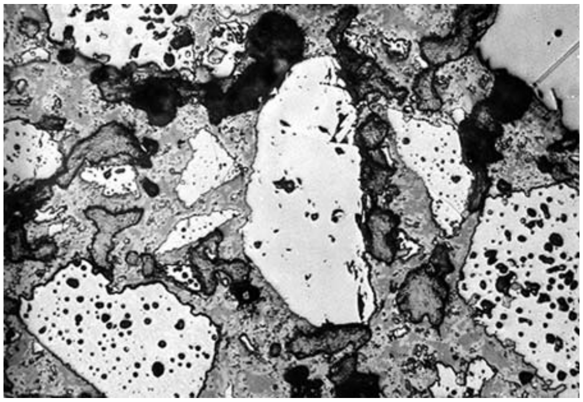
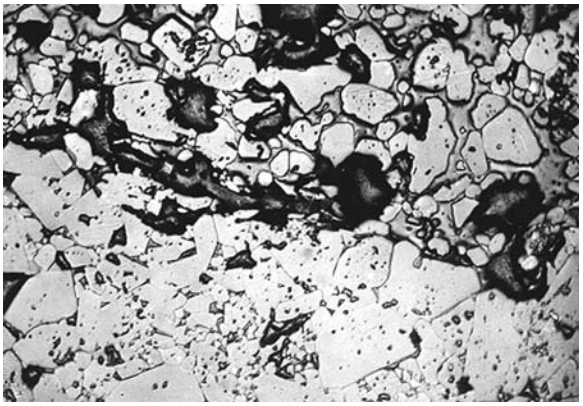


Figure 10: 90% Al_2O_3 Brick Based on Tabular Alumina Corundum Matrix



There is a practical limit on alumina content of about 96% Al_2O_3 (and 3.7% SiO_2) in refractory brick for the highest temperature applications. At compositions of higher alumina content, the products cannot be sintered in conventional gas fired kilns at sufficient temperatures to have good density and PLC (reheat) properties. While 99% Al_2O_3 class brick exist, they are primarily used for low temperature applications such as in chemical processes.

In the late 1970's, alumina-chrome brick were developed. Chromic oxide (Cr_2O_3) functions as a "sintering aid" allowing for direct bonding to be achieved at gas-fired kiln temperatures without resorting to the use of silica as a sintering aid. The end result is a more refractory product than others in the 90% Al_2O_3 class because the alumina-chrome brick only exhibit minimal SiO_2 contents. The hot modulus of rupture of these products is extremely high (Table 12). The fired alumina chrome brick are of a "ruby" red color due to the formation of an Al_2O_3-Cr_2O_3 solid solution during firing of the refractory brick.

A "spalling resistant" alumina-chrome product was subsequently developed, and it found immediate application in a number of industrial furnaces including incinerators. While the means of providing additional spalling resistance are proprietary methods, they may include use of second phases like zirconia (ZrO_2) to provide additional fracture toughness.

Selected Case Studies With Fireclay and High Alumina Brick

Reaction With Corrosive Materials at Elevated Temperature

One of the “weaknesses” of alumina-silica brick is their potential for reaction with basic slag or other corrosives to form melted phases or liquid at relatively low temperatures. The reaction potential can be illustrated by considering the reaction products expected for alumina-silica brick in the presence of lime (CaO) (Table 13).

Table 13: Melting Temperatures For Corrosive Phases With Al_2O_3-SiO_2 Brick

Corrosive Material	Reaction Product	Melting Point of Reaction Product, ^oC
Na_2O	Albite $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	1118
	Carnegite $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	1399
K_2O	Sanidinite $K_2O \cdot Al_2O_3 \cdot 6SiO_2$	1510
	Leucite $K_2O \cdot Al_2O_3 \cdot 4SiO_2$	1693
CaO	Anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$	1553
	Gehlenite $2CaO \cdot Al_2O_3 \cdot SiO_2$	1593
	Melilite $CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $2CaO \cdot Al_2O_3 \cdot SiO_2$	1280
FeO and Fe_2O_3	Iron gehlenite $2CaO \cdot Fe_2O_3 \cdot SiO_2$	1285
	Iron cordierite $2FeO \cdot 2Al_2O_3 \cdot 5SiO_2$	1210
	Fayalite $2FeO \cdot SiO_2$	1205
	Brownmillerite $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	1410
	Dicalcium ferrite $2CaO \cdot Fe_2O_3$	1449
With Al_2O_3	Calcium hexaluminate $CaO \cdot 6Al_2O_3$	1850
	Hercynite $FeO \cdot Al_2O_3$	1780

Strictly speaking, the information in Table 13 should be viewed as a "guideline" because actual melting may occur at lower temperatures than indicated by the melting points of the compound. Actual melting occurs on heating at the lowest eutectic point in the system as revealed on multi-component phase equilibrium diagrams. More information on how to estimate these initial melting temperatures is given in the chapter entitled "Corrosion". Nevertheless, the information indicates that low temperature melting is expected in the presence of certain corrosive materials.

One example is the situation where a basic slag (containing CaO) is in contact with a fireclay brick. In this situation, one might expect liquid formation near the melting point of anorthite (1553^{o}C) or melilite (1280^{o}C). In fact, melting actually is seen at about 1170^{o}C. This only illustrates that lime (CaO) is a powerful *flux* on fireclay brick. It is true that as the Al_2O_3 content of the brick increases, the relationships with CaO change. For example, lime in contact with a 60% Al_2O_3 brick would be expected to form gehlenite (melts at 1593^{o}C), but lime-silica mixtures (slags) would still form lower melting liquids even with 60% Al_2O_3 brick.

This limited discussion only points to the well-known fact that basic slags/minerals react with neutral to slightly acid Al_2O_3-SiO_2 brick resulting in corrosive wear of the refractory. The rate of the reaction differs among classes of brick with the higher Al_2O_3 brick usually exhibiting the slowest corrosion rates at elevated temperatures.

It is interesting that alumina-silica brick are attacked by acids in chemical applications at room temperature. For example, 70% Al_2O_3 brick have been known to exhibit service of only several weeks in hot hydrochloric and sulfuric acids. "Acid Proof" brick are commonly used in chemical service, and these brick last longest if they exhibit extremely low apparent porosities and if their composition exhibits extremely low alkalis. Alkali phases form glasses in manufacturing that are more readily soluble in acid media, so the bond phase in acid proof brick must contain higher alumina content and lower alkali content.

Sawdust Fired Ceramic Kiln (with Alkali Attack)

A significant number of ceramic kilns producing clay facing brick are fired with sawdust fuel in North America. It has been long recognized that wood fired boilers experience potassium attack on refractories as K_2O vapors are present in the combustion atmosphere. These vapors penetrate the refractory providing for two types of deleterious wear processes. These are (1) glazing of the brick and deposition of slag on the surface of the brick near the "burners" and (2) expansion of the brick over a long period.

In tunnel kilns of length 50-100 meters, expansion progressed over a period to the point that the interior walls made of fireclay brick typically buckle inward. In about seven years of service, the brick must be replaced to continue operation.

In the same kilns, crown (roof) brick (insulating firebrick) in flat suspended construction exhibited “sheet” spalling in seven years of service. Sheet spalling is loss of refractory thickness of about 25mm (1 inch) over a large area (many bricks). The sheet spalling was apparently a result of expansion reactions between the IFB and the alkali in the kiln atmosphere.

Rotary Kiln Application of 70% Al_2O_3 Brick and Andalusite Brick

Rotary kilns have been lined with 70% Al_2O_3 brick for many years, and a typical choice has been calcined bauxite/clay base types. These brick provide sufficient permanent expansion to keep the lining tight against the shell of the rotary kiln. This, in turn, prevents movement of brick as the kiln rotates.

The 70% Al_2O_3 class brick typically develop a “cobblestone street” appearance in service. This appearance is not necessarily an indication of an impending failure of the lining. In one instance, an inexperienced operator decided to replace the 70% Al_2O_3 brick with an Andalusite/clay brick that had “superior” spalling resistance in laboratory tests, The results was an unusually premature failure of the new lining. Because the Andalusite/clay brick had only a small permanent expansion, the brick became loose during kiln rotation resulting in progressive loss of the lining by bricks “falling out” of the lining. While the replacement of the old 70% Al_2O_3 lining was done for a few good reasons, the persons making the decision did not consider all of the criteria that contributed to many years of success with the 70% Al_2O_3 lining practice.

Incinerator Application of 70% Al_2O_3 and Alumina-Chrome Brick

Incinerator designers have used 70% Al_2O_3 brick for years in the primary and secondary combustion chambers of the kilns. For a long time, the 70% Al_2O_3 brick would experience rapid wear in the fireball regions of the secondary combustion chamber where conditions reach in excess of 1750°C. This is also an area where corrosive lime-alumina-iron oxide-silica slags coat the refractory walls.

The 70% Al_2O_3 brick were replaced with alumina-chrome brick (Table 11), and service was extended. The alumina-chrome brick initially exhibited excessive spalling loss resulting in the development of the “spall resistant” alumina-chrome brick. These latter brick have been a resounding success in incinerator service.

Health and Safety Considerations With Alumina-Silica Brick

Alumina-silica brick of 60% Al_2O_3 Class or lower (including fireclay) can contain a small amount of "free" or uncombined crystalline silica. Not all refractory brick contain free silica as its presence complicates manufacture of the brick, and certain silica phases – like cristobalite – contribute to accelerated wear.

It is well known that free silica – as quartz or cristobalite – is a respiratory hazard. Since cristobalite is the expected phase in fired alumina-silica brick, it is of the most potential concern. It is inexpensive to determine if a brick contains quartz or cristobalite. The issue is sawing of the brick during masonry construction. Wet sawing eliminates dust exposure, and it should be used if there are concerns about silica exposure.

Alumina-chrome brick can form traces of hexavalent chromium (Cr^{+6}) if the brick are used above about 1250°C and are in contact with lime rich phases. Used refractories might be checked for hexavalent chromium to ensure that any required disposal regulations are met.

References and Further Reading

References

Nishikawa, Akira, Technology of Monolithic Refractories, Plibrico Japan Company Limited (1984).
S. Aramaki and R. Roy, "Revised Phase Diagram for the System Al_2O_3-SiO_2", J. Am. Ceram. Soc., 45 (5) 2290242 (1962).
Rex W, Grimshaw, The Chemistry and Physics of Clays, Techbooks (1971).

Further Reading

For General Information on Refractories:
Kirk-Othmer, "Refractories" in Encyclopedia of Chemical Technology, 20, 1-37 (1982, or most recent edition).
Refractories Manual, The American Foundrymen's Society (1989).
For Technical Information on Clay, Alumina and Mullite
"Structural Oxides I: Al_2O_3 and Mullite", in Ceramic Microstructures, William F. Lee and W. Mark Rainforth, Chapman and Hall (1994).
Alumina as a Ceramic Material, Special publication No. 4, The American Ceramic Society (1970).
"Microstructure of Complex Ceramics" in Ceramic Microstructures, R. Fulrath and J. Pask, Krieger Publishing Company (1976).
For Historical Information
Refractories: The Hidden Industry, The American Ceramic Society (1987).