

Introduction to Refractory Materials

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The Aim of the Course



What we will learn?

- *What is a refractory?*
- *Why required?*
- *Who is using these materials?*
- *Role of refractories in materials science*
- *Engineering properties of refractories*

Refractory Materials in Engineering

- Properties required in a refractory
- Fracture of Refractories
- Alumina-Silica Bricks (AKA Mullite)
- Magnesite Refractories
- Silica Brick Material Properties
- Dolomite Refractories
- Carbonaceous Refractories
- Spinel-Containing Refractories
- Surface Chemistry as a Tool for the Development of Advanced Refractory Castables
- Refractory Applications in Refineries and Circulating Fluid Bed Reactors
- Testing of Refractory Materials



Course Frame

2 Mid-Terms

1 Final

Homeworks

Attendance

13 Weeks

16 Headlines

2 Technical Visits



Take Notes!

The lesson won't be through the slides only

Introduction to Refractory Materials*

* High heat resistant Ceramics (?)



Refractories are materials that resist high temperatures, liquid slags and aggressive atmospheres, and do not change form (e.g., burn or melt) in service, They are nameless heroes of high temperature process industries



What is a Refractory?

- Refractories are inorganic nonmetallic materials resistant to heat and are exposed to different degrees of mechanical stress and strain, thermal stress and strain, corrosion/erosion from solids, liquids and gases, gas diffusion, and mechanical abrasion at various temperatures
- Different refractories are designed and manufactured so that the properties of the refractories will be appropriate for their applications.
- Different refractories are designed and manufactured so that the properties of the refractories will be appropriate for their applications.
- Refractories are broadly divided into two categories—shaped (bricks and cast shapes) and unshaped (monolithic) refractories.

Why **Refractories** are Required?



- To minimize heat losses from the reaction chamber
- To allow thermal energy dependent conversion of chemically reactive reactants into products because metallic vessels are not suitable.
- i.e; in steelmaking, the physico- chemical properties of the following phases are important:

Slag: Mixture of acidic and basic inorganic oxides like SiO_2 , P_2O_5 , CaO , MgO , FeO , etc.; temperature varies in between 1400°C to 1600°C . , **Refractories are required**

Molten steel: Iron containing carbon, silicon, manganese, phosphorous, tramp elements, non metallic inclusions, dissolved gases like nitrogen, oxygen and hydrogen and different alloying elements like Cr, Ni, Nb, Mo, W, Mo etc.; temperature 1600°C **Refractories are required**

Gases: CO , CO_2 , N_2 , Ar containing solid particles of Fe_2O_3 , Fe_3O_4 etc.; temperature 1300°C to 1600°C
Refractories are required

Who is using **Refractory** Materials?



- Basic Oxygen Furnaces (BOF) using industries, i.e; Cast Iron
- Electric Arc Furnaces (EAF) using industries, i.e; Steel
- Ladle Metallurgical Furnaces (LMF) i.e; Alloys
- Aluminium producers seeking to avoid contamination in high temps.
- Hydrocarbon industries, ie, petrochemical refining, abrasion in high temps.
- Glass producers, non porous refractories are needed/used
- Ceramic producers, insulation during sintering process



What are the **Refractory** Requirements?

- The diversified applications of refractory materials in several different types of industries require diversified properties to meet the physico-chemical and thermal requirements of different phases. In some industrial units more than one phase are present e.g. in steel-making vessels slag /metal /gases/glasses are simultaneously present in the vessel at high temperatures. In the heat treating furnaces solid/reducing or oxidizing gases are simultaneously present. High temperature resistance.
- **Refractoriness:** Refractoriness is a property at which a refractory will deform under its own load. The refractoriness is indicated by PCE (Pyrometric cone equivalent). It should be higher than the application temperatures. Refractoriness decreases when refractory is under load. Therefore more important is refractoriness under load (RUL) rather than refractoriness.
- **Porosity and Slag permeability:** Porosity affects chemical attack by molten slag, metal and gases. Decrease in porosity increases strength and thermal Conductivity.



What are the **Refractory** Requirements?

- **Strength:** It is the resistance of the refractory to compressive loads, tension and shear stresses. In taller furnaces, the refractory has to support a heavy load; hence strength under the combined effect of temperature and load, i.e. refractoriness under load is important.
- **Specific gravity:** Specific gravity of the refractory is important to consider the weight of a brick. Cost of bricks of higher specific gravity is more than that of lower specific gravity. But strength of bricks of higher specific gravity is greater than one with lower specific gravity
- **Spalling:** Spalling relates to fracture of refractory brick which may occur due to the following reasons:
 - A temperature gradient in the brick which is caused by sudden heating or cooling.*
 - Compression in a structure of refractory due to expansion*
 - Variation in coefficient of thermal expansion between the surface layer and the body of the brick*
 - Variation in coefficient of thermal expansion between the surface layer and the body of the brick is due to slag penetration or due to structural change.*



What are the **Refractory** Requirements?

- On sudden heating

$$\text{Spalling tendency} \propto \frac{\text{coeff. of thermal expansion}}{\text{max}^m \text{shearing strain} \sqrt{\text{thermal diffusivity}}}$$

- On sudden cooling

$$\text{Spalling tendency} \propto \frac{\text{coeff. of thermal expansion}}{\text{max}^m \text{tensile strength} \sqrt{\text{thermal diffusivity}}}$$



What are the **Refractory** Requirements?

- **Permanent Linear change (PLC) on reheating**

In materials certain permanent changes occur during heating and these changes may be due to;

Change in the allotropic form

Chemical reaction

Liquid phase formative

Sintering reactions

$$\text{PLC}(\%)_{\text{linear}} = \frac{\text{Increase /decrease in length}}{\text{original length}} \times 100$$

$$\text{PLC}(\%)_{\text{volume}} = \frac{\text{Increase /decrease in volume}}{\text{original volume}} \times 100$$

These changes determine the volume stability and expansion and shrinkage of the refractory at high temperatures.



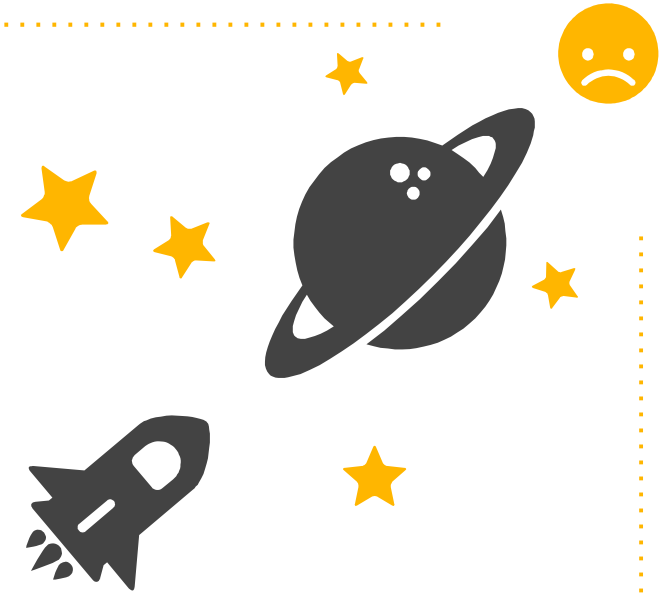
What are the **Refractory** Requirements?

- **Bulk density:** Decrease in bulk density increases volume stability, heat capacity.

The First Homework

Please write an essay about «*Role of refractories in materials science & engineering*»

Min. 800 words



Properties of Refractory Materials*

Physical – Chemical - Thermal



Refractory Properties can be classified as follows;

- **Physical**

Density
Porosity
Strength
Abrasion

- **Thermal**

Thermal shock
Thermal conductivity
Thermal diffusivity

- **Chemical**

Corrosion/erosion

- **Ceramic**



Physical Properties

- Physical property requirements for shaped and unshaped refractories are different.
- For shaped refractories, the main requirements are their density, porosity and dimensional tolerance
- Monolithic (unshaped) refractories have to be characterized with different parameters
- For plastics refractories, the workability and aging characteristics are the prime requirements, whereas, for ramming mixes, the rammability with proper compaction is the main requirement
- For castable/pumpable refractories, the prime requirement is the flowability at a specific water addition with or without vibration
- Refractory materials are characterized by their physical properties, which often indicate the use and performance of refractory materials, ASTM (1) Tests.



Physical Properties

Density and porosity (ASTM D-20)

- The values of density and porosity determined by standard methods are used to recommend or predict the use of refractories for specific uses.
- The higher the density, the lower the porosity.
- Other physical properties, such as strength, abrasion, and gas permeability, are often related to the density and porosity of the refractory.



Physical Properties

Strengths. *Cold and hot, their importance*

- The physical strengths, in both cold and hot conditions, are often characterized as measures of the use of a refractory
- Cold strengths indicate the handling and installation of the refractory, whereas hot strengths indicate how the refractory will perform when used at elevated temperatures
- Initial strength develops in refractory materials during the forming process
- For shaped refractories, the strengths often develop during the physical processing of the products and sometimes followed by higher temperatures where the refractory goes through a firing process
- For monolithic refractories, the initial strength develops during the installation or forming process (for precast shapes), and the final strength develops while in application.
- Strengths of refractories are measured as cold compressive strength, cold modulus of rupture, or hot modulus of rupture. Hot modulus of rupture provides the best indication of the performance of a refractory material in use.



Physical Properties

Cold Compressive Strength (ASTM C-133).

- The cold compressive strength of a refractory material is an indication of its suitability for use of refractories in construction. It is a combined measure of the refractory for the strength of the grains and also of the bonding system.

Cold Modulus of Rupture (ASTM C-133)

- The cold modulus of rupture of a refractory material indicates the flexural strength and its suitability for use in construction. It is indicative of the strength of the bonding system of the refractory product. Since the test is done at room temperature, it can only show its Properties of Refractories 5 suitability and its use in construction. It provides no indication of how the refractory will behave at elevated temperatures.



Physical Properties

Hot Modulus of Rupture (ASTM C-583)

- The hot modulus of rupture provides the indication of a refractory material about its flexural strength at elevated temperatures.
- Since refractories are used at elevated temperatures, the hot modulus of rupture is the true indicator of the suitability and performance of a refractory at high temperatures.
- In recent years, the hot modulus of rupture has been prescribed and required by users as the most important test criterion for selection and use of refractories.



Physical Properties

Abrasion Resistance (ASTM C-704)

- This is a measure of the resistance of a refractory material when high-velocity particles abrade the surface of the refractory.
- It measures the strength of the bond and the refractory particles and its resistance to the flow of high-velocity particles across its surface.
- The need for good abrasion resistance of refractory materials is most evident in petrochemical industries where fine particles impinge the refractory surface at high velocities at moderately elevated temperatures.
- A direct correlation between abrasion resistance and cold crushing strength has recently been established.
- The cold crushing strengths can provide, and have a direct indication about, the predictability of a refractory material regarding its resistance to abrasion.



Thermal Properties

Thermal Expansion

- This is a measure of the refractory about its linear stability when it is exposed to different ranges of high temperatures and then cooled to room temperatures.
- It is defined as a permanent linear change (ASTM C-113) and is measured by the changes in the longest linear dimensions.
- **Most refractory materials expand when heated**



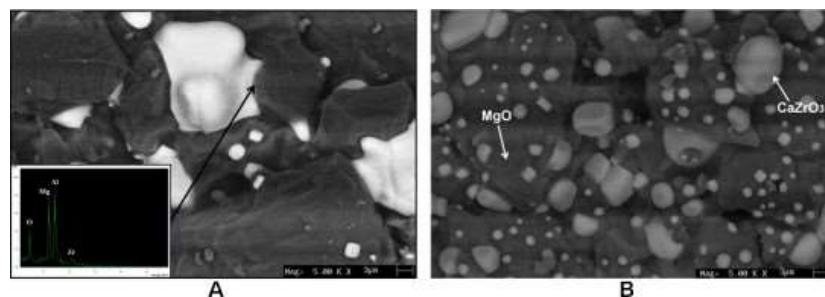
When refractories are installed at room temperatures, the whole structure tightens up when heated. But if the temperature reaches higher than the softening temperature of the bonding system, the structure may distort or collapse. Hence, refractory systems should always be designed in such a way that the maximum temperature attainable in the system is lower than the softening or melting temperature of the refractory ingredients (grains and bonding system). Often cracks are observed in monolithic refractory systems when cooled, but, in most cases, the apparent cracks visible on cooling close up after the system is heated up.



Thermal Properties

Thermal Shock

- This is measure of the refractory property when the refractory is exposed to alternate heating and cooling, It is an important property for a refractory material.
- Most high-temperature processes experience heating and cooling. Both refractory grains and the bonding system expand while being heated and contract during cooling.



Example: MgAl_2O_4 spinel as an effective ceramic bonding in a MgO - CaZrO_3 refractory
<https://doi.org/10.1016/j.jeurceramsoc.2013.04.027>



Thermal Properties

Thermal Shock

- Refractories having structures with built-in microcracks or defects show better thermal shock resistance than with rigid systems.
- In some refractories, the bonding system, by nature, possesses microstructural defects or cracks that provide better thermal shock resistance.

There are two standard methods for determining the thermal shock resistance of refractory materials;

- For brick shapes, thermal shock resistance is measured by "Ribbon Thermal Shock Testing" (ASTM C-1100)
- For monolithic refractories the standard method is ASTM C-1171.
- These tests clearly differentiate among refractory materials about their resistance to thermal shocks.



Thermal Properties

Thermal Conductivity

- Thermal conductivity is a measure of the refractory regarding its ability to conduct heat from the hot to the cold face when it is exposed to high temperatures.

There are three different methods of determining thermal conductivity of refractory materials. ASTM C-210 is the standard method for determining thermal conductivity of refractories;

- ASTM C-202 is the standard method for determining thermal conductivity of refractory brick; and ASTM C-1113 is the standard method for determining thermal conductivity of refractories by hot wire.
- The thermal conductivity tests are particularly important for insulating refractories where the thermal gradients from the hot face to the cold face dictate the use of a refractory material for the specific uses.



Thermal Properties

✦ Which type of thermal property is needed?

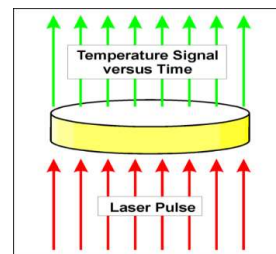
- a) For steel production
- b) For ceramic production



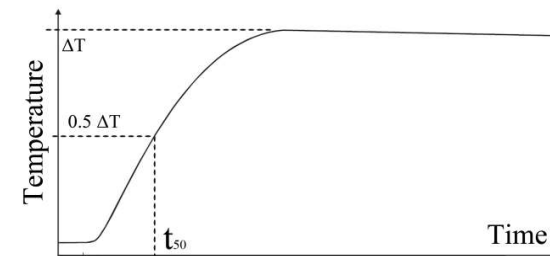
Thermal Properties

Thermal Diffusivity

- Thermal diffusivity α (mm²/s) is a measure of thermal inertia of a material. It gives an insight of how fast heat is propagated through the medium. The Pulse (flash) method was primarily developed to measure this value.
- The thermal diffusivity property is particularly useful for carbon-containing materials. ASTM C-714 is the standard method for determining thermal diffusivity of carbon and graphite by the thermal pulse (flash) method.



Principle of the laser flash method.



Typical curve of temperature vs. time.



Chemical Properties

- The chemical properties of a refractory are defined by the chemical analysis of the refractory grains, by the nature of the bonding, and also by the ability of the refractory to resist the action of liquids when exposed to high temperatures
- The chemical properties of a refractory material are primarily dictated by the chemical composition of the refractory
- The bonding system of the refractory plays a vital role in dictating its properties
- When refractories are exposed to corrosive liquids at high temperatures, the extent of corrosion/erosion depends on the refractory grains and the chemical bonding system of the refractory
- Refractory corrosion may be caused by mechanisms such as dissolution in contact with liquid, a vapor –liquid or solid-phase reactions

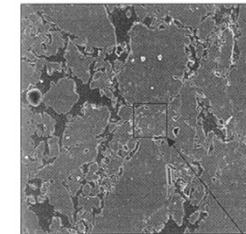


FIG. 1c

ZrO₂ – 67.91%
CaO – 30.20%
MgO – 1.90%

Al₂O₃ – 75.17%
MgO – 24.83%

MgO – 99.32%
CaO – 0.12%
SiO₂ – 0.11%
Fe₂O₃ – 0.45%

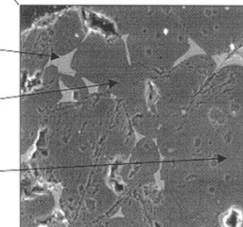
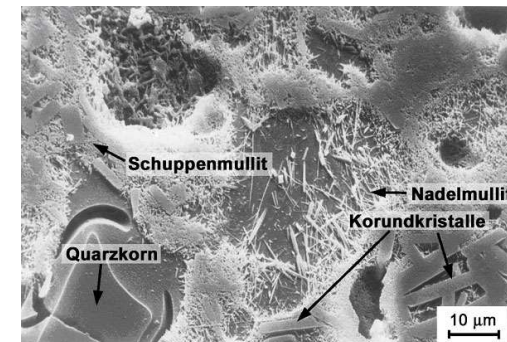


FIG. 1d



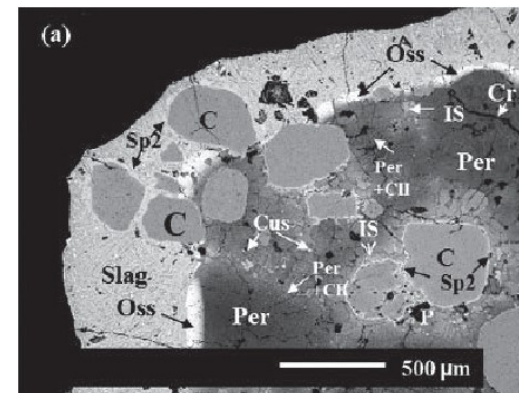
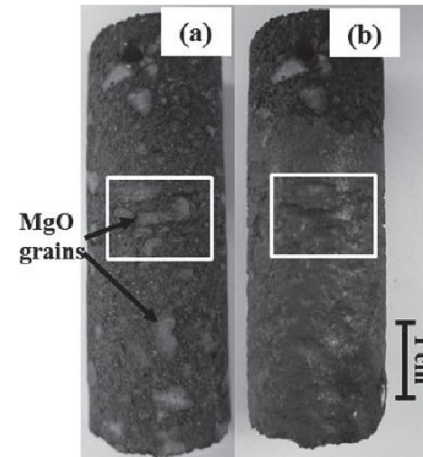
Chemical Properties

- It may also occur due to penetration of the vapor or liquid in the pores, resulting in an alternate zone. In most cases, corrosion is the result of some combination of these aforementioned factors



In metallurgy;

A concentration gradient occurs in the refractory composition at the boundary region when the refractory comes in contact with the molten slag. The refractory components diffuse through the interfacial film and dissolve in the liquid. The interfacial film influences the rate of dissolution. The larger the concentration gradient, the faster the dissolution rate and thus the refractory dissolves more readily.





Chemical Properties

- Corrosion/erosion resistance is one of the most important characteristics of refractories, which are exposed to molten metal and slag. Hence, the design of the tests closely simulating the conditions that they are exposed to is crucial.
- During the formulation of a refractory, close attention is given to a refractory composition in choosing the refractory grains and the bonding system. Thus, refractories used in an iron-making process will differ from that of a steel-making process since the nature of the metal and slag is different in these cases.
- In iron making, the metal and liquid slag is primarily neutral or slightly acidic in nature, whereas the slag is distinctively basic in the steel-making process. Refractories chosen for iron making are based on alumina and silica, whereas magnesia-base refractories are the choice for steel making.
- The exposure of refractories to molten metal/slag is a dynamic process, the tests simulating the conditions also need to be dynamic. For steelmaking refractories, the rotary slag test (ASTM C874) provides close simulation of the conditions in steel-making refractories.

Chemical Properties



Processes

Steelmaking

Ironmaking

Cement

Non-Ferrous

Glass

Lead

Cu/Ni

Aluminum

Materials

Forsterite

Mag-Chrome

Chromite

Mullite

Doloma

Crome-Mag

Corundum

Zircon

Magnesia

Chromic Oxide

Firebrick

Silica

Zirconia





Ceramic Properties

- Ceramic properties of a refractory material are defined by its nature or reaction when exposed to heat
- Refractories behave differently when exposed to heat, depending on the type of the refractory and how it has been formed. For fired bricks, the ceramic reactions and bonds have already been instituted by high-temperature firing. Hence, when they are exposed to high temperature, they do not exhibit any further change
- However, for unfired refractories, the formulations are designed so that the ceramic reactions are supposed to take place at those temperatures. Thus, for fired bricks like fireclay, high-alumina, magnesia-chrome-type bricks, which are already fired at high temperatures, do not exhibit any further ceramic reaction when exposed to high temperatures





Ceramic Properties

- For unfired refractories, like magnesia-carbon bricks and alumina-carbon bricks, the formulations are designed so that the ceramic properties will be developed at use temperatures
- For monolithic refractories, the formulations are made so that the ceramic properties develop when they are exposed to high temperatures. Monolithic refractories, like plastics, ramming mixes, dry vibratables, mortars, and coatings, Properties of Refractories 9 are already prepared and are to be applied as received
- Recent developments in low- and ultralow-cement castables/pumpables, the effects of the ultrafine particles are of great significance.





Ceramic Properties

- In recently developed refractories, the water requirements are low since the ultrafine silica fume particles (mostly used in these compositions) occupy part of the space of water.
- Although the silica fume helps in reducing water requirements in the castable, it affects high-temperature properties due to the formation of anorthite and gehlinite phases at temperatures around 1250°C – 1400°C.



Fracture of Refractories

REFRACTORY STRENGTHS - THE FRACTURE TOUGHNESS/STRENGTH RELATIONSHIP
THERMAL STRESS FRACTURE - NONLINEAR FRACTURE AND THE J-INTEGRAL APPROACH
WORK-OF-FRACTURE

Fracture of Refractories



- Fracture has always been a critical problem for refractories during their use. It has not been a field that is without progress, as can be appreciated by referring to previous reviews in academic database
- The composite nature of refractories separates the refractory fracture process from that of single-phase, fine grain size, high-strength brittle structural ceramics and more closely associates refractory fracture with the fracture of engineering composite materials

i.e; similar to high-tech composites, refractories generally exhibit rising R-curves during crack extension or propagation*

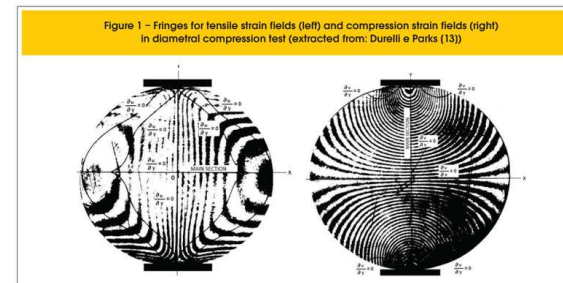
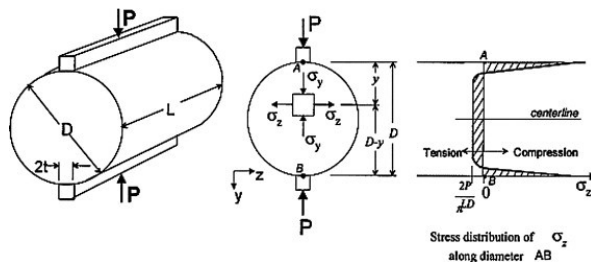
R-curve* behavior is characterized by an increase in crack resistance (toughness) with crack extension

- Fracture is one of the two most common modes of failure for the refractory linings of modern industrial processing vessels. The other is chemical attack, or corrosion by the material that the refractories are containing within the process vessel, often molten metals or glasses at very high temperatures
- Fracture failures of refractories are of several varieties, including simple mechanical overload as may develop from impact during the loading of the 12 Bradt process vessel with scrap metal
- Thermal stress fracture during cooling or heating, particularly the initial heat-up of a vessel or during rapid thermal cycling between heats, is another type of failure

Fracture of Refractories

Refractory Strengths

- Strengths of refractories are usually reported in terms of the three-point bend strength or the flexural strength, frequently called the modulus of rupture (MOR)
- In the case of refractories, there exists a standard test for this simple strength measurement. It is based on the familiar formula: $\sigma_f(\text{MOR}) = 3PL/2bh^2$ where σ_f is the strength in three-point bending, L is the length of the test span, b is the specimen width, and h is the specimen height. The fracture load is P, It specifies the tensile stress at the bottom of the flexing bend test beam. (Eq 1)
- Some researchers have developed an appreciation for another strength test, the Brazil test. In that test a cylindrical specimen is diametrically loaded in compression to produce an internal tensile failure aligned with the specimen diameter.



Fracture of Refractories

- In principle, Eq. (1) is strictly applicable only when the load-displacement curve is fully linear elastic to failure, similar to the middle diagram in Figure 1, which illustrates an unnotched J-integral measurement test specimen. Unfortunately, only rarely are the load-displacement curves determined during the normal strength measurements of refractories.



Refractories are utilized at elevated temperatures, so there is naturally an interest in the change of their strength with increasing temperature. When the strength of refractories is measured by the three-point bend test and done so as a function of temperature, the bend or flexural strength invariably exhibits a maximum that is associated with the softening of the silicate bonds. This strength maximum is usually not a very large one. It is usually observed between 600°C and 1400°C, depending on the particular refractory type, its silicate content, and the specific chemistry of that silicate. At more elevated temperatures, above this strength maximum, the strength of the refractory rapidly decreases!

J-integral : the curve in high plastic deformation
Elastic and plastic are measured deformation together

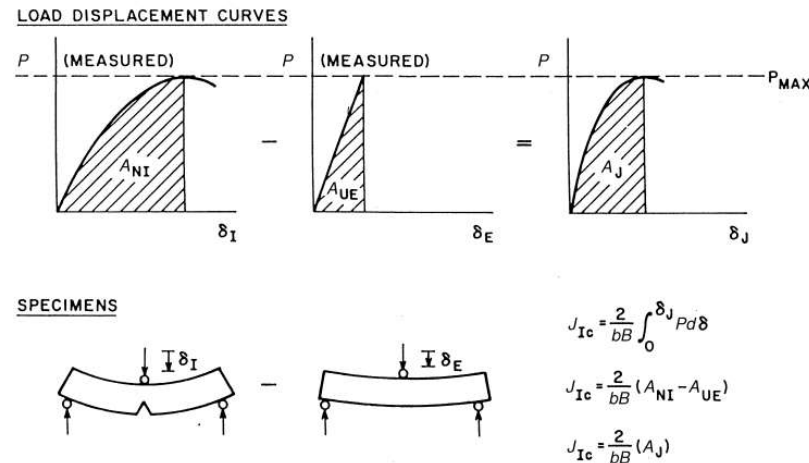


Figure 1 The illustrated compliance technique for J-integral determination. (From Ref. 18.)



Fracture of Refractories

The Fracture Toughness/Strength Relationship

- The rather low fracture toughness values for refractories are to be expected, for refractories are not very strong and their intrinsic flaws are quite large, as evidenced by the readily visible large aggregates (flaws) in refractory bodies.
- Although the fracture toughness is by no means the complete situation for the fracture of refractories, its low values clearly send the message that the crack initiation resistance of refractories is not very large.
- Cracking and fracture may be expected to be of concern for industrial refractories in many of their applications.



Fracture of Refractories

Thermal Stress Fracture

- When fracture occurs as a consequence of the thermal stresses generated during the temperature changes that a refractory lining experiences during its initial heating, or during thermal cycling of day-to-day operational practices, the extent of damage during fracture is governed by an energy criterion
- The thermal stress damage resistance decreases as the strength increases
- Refractory engineering pioneers often expressed the thought that the large hard aggregates acted as thermal shock crack stoppers
- Now it is recognized that the strong large aggregates also assume an important role in the creation of a rising R-curve in refractories and will decrease the extent of crack propagation, a point discussed later. No matter how multifaceted the role of the aggregates may be, it is now obvious that where thermal shock damage resistance is a concern, then a stronger refractory is not necessarily a better refractory.



Fracture of Refractories

Nonlinear fracture and The J-Integral Approach

- Linear elastic, brittle fracture of refractories occurs only at room temperature, or at moderately elevated temperatures. Even at room temperature, many refractories, especially castables or other monolithics, will exhibit an extensive nonlinear portion of the load-displacement curve prior to failure in a normal bend strength test, and most certainly in a fracture mechanics test with a large artificial crack.
- This nonlinear form is the result of inelastic phenomena occurring in the region of the crack or fracture, both in the crack front process zone ahead of the main crack (microcracking) and also in the following wake region behind the crack front across the newly formed fracture surfaces (aggregate bridging).
- After the usual linear elastic region during initial loading, an extensive bending of the curve occurs and a nonlinear region develops that soon reaches a maximum value in the load-displacement curve.
- This general load-displacement characteristic of nonlinearity also occurs for many metals, but it is a consequence of the extensive plastic zone that develops surrounding the crack tip frontal region during yielding and dislocation plastic flow. The point is that the nonlinear stress-strain or load-displacement curve is a general load-displacement phenomenon in many materials, one that is not restricted to only industrial refractories.

Corrosion of Refractories

Principle on Refractory and Slag Compatibility - Principle on Porosity and Corrosion Rates
Principle on Reactions and Temperature Gradients - Thin Wall - Thick Wall



Corrosion of Refractories

- Refractories are used at elevated temperatures for structural purposes, and they are used in many cases to contain a high-temperature corrosive environment.
- This corrosive environment usually contains liquid (melted) phases that participate in chemical reactions with the refractory at elevated temperatures resulting in refractory consumption or wear. It is usually not immediately obvious, but the oxidation and reduction state of the environment (as “redox” conditions or oxygen “activity”) can participate in and influence the chemical reactions that take place. Along with chemical reactions during corrosion, physical changes occur that may be accelerated by the corrosion process.
- It is an essential point that corrosion reactions proceed in a direction toward localized chemical equilibrium. This means that phase equilibrium diagrams can be used to analyze corrosion situations and to predict chemical strategies to minimize corrosion and wear rates.
- This gives persons interested in refractory corrosion two options. The first is to view corrosion as a chemical and physical process without a detailed application of phase equilibrium diagrams—called the “phenomenological approach.” The second is to use the information in the phenomenological approach and to use phase equilibrium diagrams. This latter option is required for a full understanding of refractory corrosion.

Corrosion of Refractories



First Fundamental Principle on Refractory and Slag Compatibility

The first fundamental principle is that “acid” refractories tend to resist “acid” slags better than “basic” slags and, conversely, “basic” refractories tend to resist “basic” slags better than “acid” slags. The definitions of acidity and basicity in room-temperature solution chemistry and of refractory chemistry at elevated temperature have a key difference.

Definition of Acidity and Basicity in Solution Chemistry at Room Temperature

An acid contains an excess of hydrogen ions (H^+) over hydroxyl ions (OH^-) considering a “baseline” defined as neutrality (a “pH” of 7.0). An acidic substance contributes hydrogen ions to a chemical solution to make it more acidic, whereas a basic substance contributes hydroxyl ions to make it more basic.

Corrosion of Refractories



Definition of Acidity and Basicity in Corrosion Chemistry at Elevated Temperature

An acidic material contains an excess of silica content (SiO_2) over basic materials (usually CaO) considering a "baseline" defined as neutrality (a CaO/SiO_2 ratio of 1.0). An acidic material contributes SiO_2 in a corrosion reaction, whereas a basic material contributes CaO or MgO in a corrosion reaction. This leads to the observation that acid refractories are more "compatible" with acid slags, that is, acid materials experience less corrosion loss against acid slags as compared to basic slags. In a like manner, basic refractories are more compatible with basic slags than with acid slags.

Corrosion of Refractories



Second Fundamental Principle on Porosity and Corrosion Rates

Most refractories contain void space or porosity. This porosity may be open pores that can be penetrated by a fluid media (i.e., "apparent" porosity) and/or it may be closed porosity that is not easily penetrated by fluid media. If a refractory contained no porosity (or brick joints, expansion joints, or construction joints), the corrosion reaction is limited only to the face exposed to the corrosive media (called the hot face). When porosity is present, particularly when open porosity is present, the corrosive media can penetrate the refractory, causing destructive reactions behind the hot face.

Most investigators have found that slag corrosion rates increase linearly with the percentage of apparent porosity within the refractory. This is usually true within a limited range of apparent porosity—for example, in the range 12–16% apparent porosity—but it is not necessarily true at high apparent porosities (.20%).

Corrosion of Refractories

Third Fundamental Principle on Reactions and Temperature Gradients

A key concept of this principle is that the temperature gradient affects the extent of phenomena seen in slag corrosion. In a very steep temperature gradient, very little penetration of slag is seen, with corrosion reactions more or less restricted to the immediate slag and refractory interface. Mobility of fresh slag (reactant) to the slag–refractory interface may be limited, and transport of reaction products away from the slag–refractory interface may be slow. Steep gradients are seen in thin-wall refractory linings such as those used in utility boilers featuring water or steam cooling at the furnace shell.

In conventional refractory designs, the lining is at least one brick thickness (.225 m), and the lining typically features a safety lining for a total thickness of at least 450 mm. The slag freeze plane may be located in a zone of 40–75 mm behind the hot face. In some cases, slag may penetrate up to 150 mm behind the hot face.

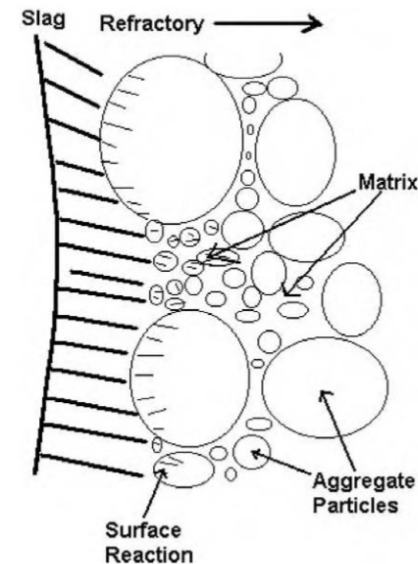


Figure 2 Stage I of slag attack (showing a bonded refractory).



Corrosion of Refractories



EQUILIBRIUM CONSIDERATIONS AND PHASE DIAGRAMS

A phase diagram is a map showing equilibrium phases present as a function of composition and temperature. The phase diagram essentially shows the melting relationships in a given chemical

Even without a complete understanding of phase diagrams, they can be used in a "simplified method" to analyze corrosion. This method provides a "first approximation" of the corrosion potential of the system. This technique will be illustrated using the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (Figure 5). In the chapter on alumina-silica brick, two consequences of Na_2O exposure are mentioned for alumina-silica brick including "glazing" (corrosion to form melted phase) and expansions. This discussion will only consider corrosion of the refractory to form liquids during corrosion.

Corrosion of Refractories



The first step is to locate the point on the diagram representing the refractory main constituents. For this discussion, we will use a 40% Al_2O_3 superduty brick in contact with a corrosive phase consisting of 20% Na_2O and 80% SiO_2 . Both these compositions are indicated in Figure 5 indicating the approximate composition of the slag and another circle indicating the approximate composition of the brick (on the Al_2O_3 - SiO_2 composition line or "join").

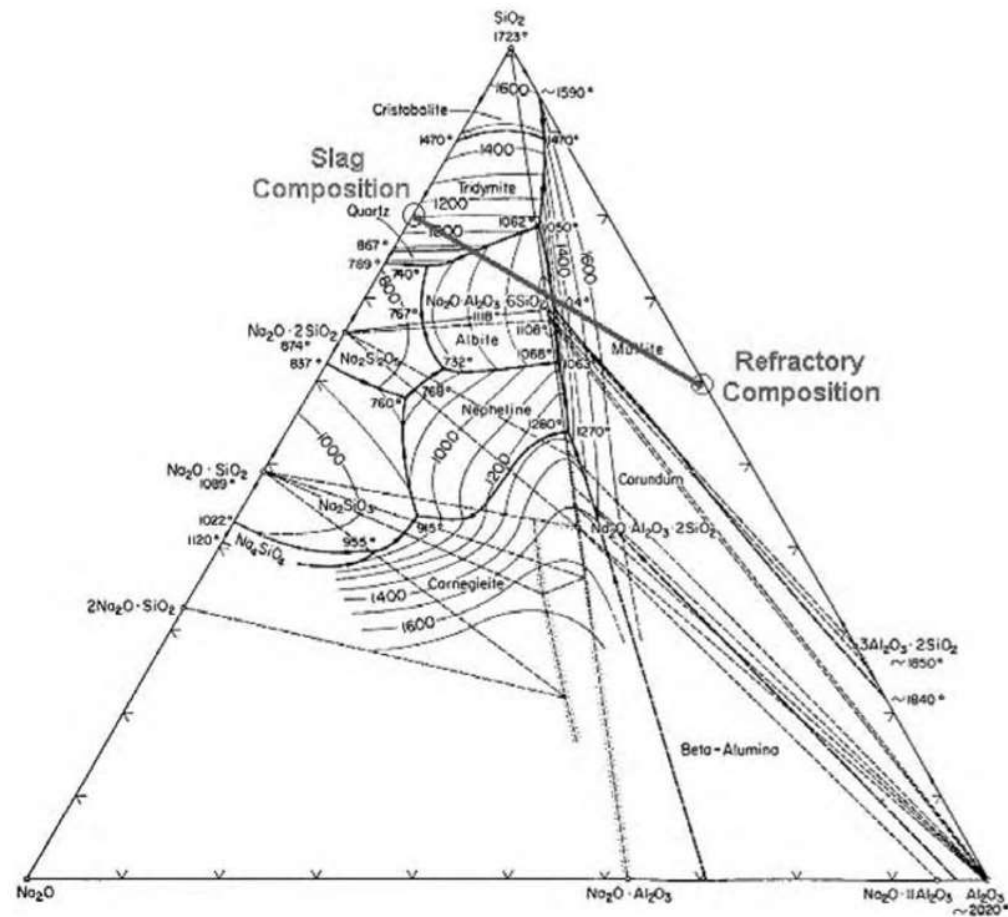


Figure 5 $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ phase diagram used in a corrosion example.



The second step is to draw a line between the slag composition and the brick composition (indicated in Figure 5). It is essential to recognize that all potential reaction products between the refractory and the slag at equilibrium must be located on the line in Figure 5 joining refractory and slag compositions. The analysis of the corrosion potential is as follows:

1. At the slag–refractory interface, the composition must move from that of the refractory in a direction toward the composition of the slag, i.e., the local composition moves in a “northwesterly” direction.
2. The compound at equilibrium between the slag composition and the refractory composition is “albite,” or $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, melting at 1104°C . Therefore, at equilibrium, the localized melting point of corrosion products at the hot face is 1104°C . Note that albite is contained in the “compatibility” triangle between SiO_2 , mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), and albite. The compatibility triangle establishes the phases that may be present at equilibrium. Mullite and SiO_2 (as glass or vitrified phase) are intrinsic to the refractory. Albite is formed as a consequence of corrosion reactions.
3. The line joining the refractory and the slag crosses temperatures as low as about 1000°C . This implies that nonequilibrium liquids could be formed at this low temperature during corrosion. In Stage I of corrosion, such nonequilibrium liquids are expected. Only in Stage II of corrosion will sufficient refractory be dissolved in the slag to allow observation of the equilibrium corrosion product.



4. The line joining the refractory and the slag composition crosses the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ – SiO_2 – $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ compatibility triangle near the ternary (3 component) eutectic or lowest melting temperature of 740°C. This implies that liquids melting as low as 740°C could be formed during nonequilibrium conditions. Considerable qualification is needed when performing this type of analysis. One is that the refractory contains other components than Al_2O_3 and SiO_2 —notably fluxes like K_2O and Fe_2O_3 . These components can lower the melting points predicted by the diagram. Additionally, the slag may contain other components, changing the melting relationships.

CASE STUDIES OF CORROSION



Alumina-Silica Brick in Ferrous Foundry Applications

Slag used in ferrous foundry applications is found to contain lime (CaO), silica (SiO_2), iron oxide (FeO), and other oxide constituents. As a first approximation, the slag can be assumed as a binary mixture of alumina and silica as they are usually the major components of the slag. The major components of the brick can be represented using the binary Al_2O_3 – SiO_2 phase diagram, and this allows the corrosion situation to be analyzed using the three-component CaO – Al_2O_3 – SiO_2 phase diagram

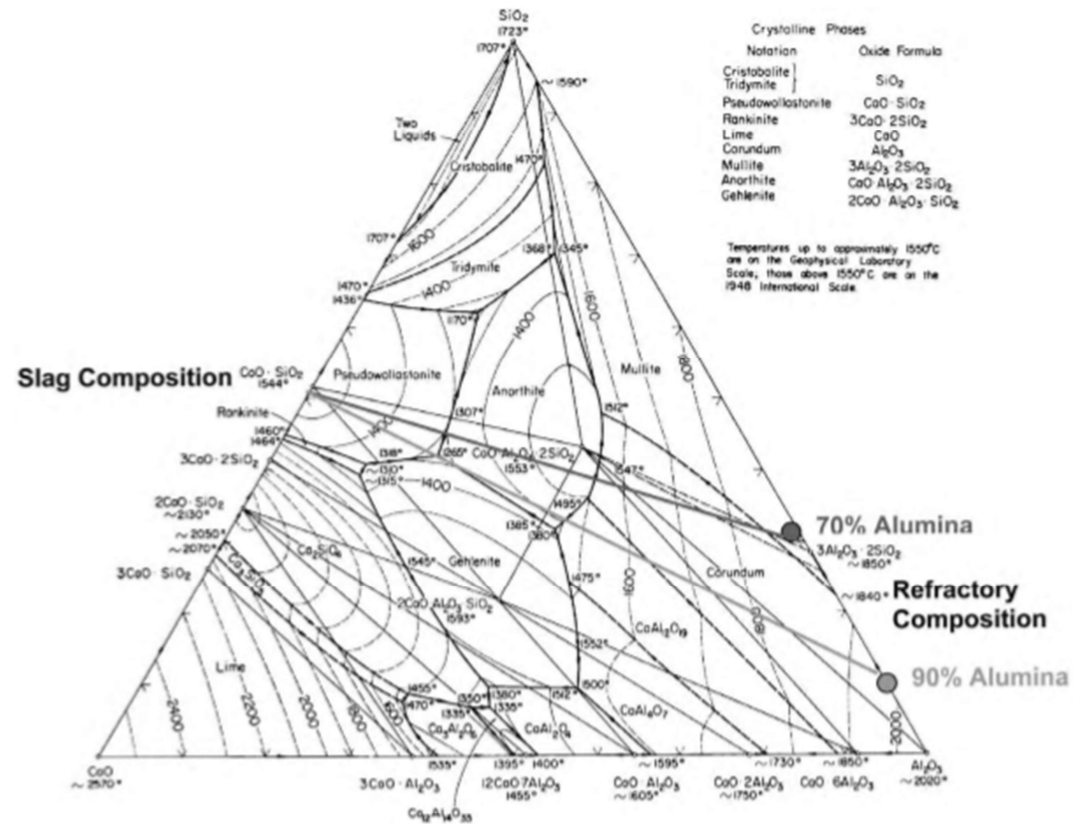


Figure 7 Representation of corrosion of alumina-silica brick in foundry/steel-making slag.



Cases of corrosion of 70% Al_2O_3 and 90% Al_2O_3 brick are analyzed in previous slide using Figure 7.

The composition of the brick is plotted on the Al_2O_3 – SiO_2 binary (two-component) side of the diagram. Then, a line is drawn to the expected slag composition using the average CaO/SiO_2 ratio of the slag. For this discussion, the slag is assumed to have a CaO/SiO_2 ratio of 1.0. A few things are very clear on looking at the lines joining the brick composition and the slag composition in Figure 7:

1. Both “joins” between brick and slag pass very close to the ternary eutectic at 1265C, implying that the slag and refractory compositions will produce liquid phases, i.e., exhibit corrosion, whenever they are in intimate contact and when this temperature is reached. Other fluxing oxides typically reduce this temperature by as much as 508C.
2. The effect of lime- (CaO) rich phases penetrating the brick is to render the mullite “binder” in the refractory as a nonequilibrium phase, i.e., the binder is dissolved into the penetrating slag phases and corrosion products. In 70% Al_2O_3 brick, the mullite is stable until the local composition reaches 20% CaO , while in 90% Al_2O_3 brick, the mullite disappears when the local composition reaches 8% CaO . The phase diagram has provided a first approximation of the reaction temperature between the slag and refractory for corrosion to begin, i.e., when the liquid phase is produced as a product of corrosion reactions.



The joins between refractory composition and slag composition in Figure 7 could have been constructed to analyze the situation with higher slag basicity, i.e., CaO/SiO_2 of 1.5 or 2.0. In this situation, the lines would cross close to the ternary peritectic at 1380°C. This eutectic mixture between anorthite and gehlenite has the special name of “melilite.” The binary join between anorthite and gehlenite is shown in Figure 8, where it is easier to see the solidus temperature, or the temperature above which corrosion begins. Thus, higher $\text{CaO}-\text{SiO}_2$ ratios increase the initial reaction temperature between the slag and refractory with respect to formation of liquid phases and the beginning of corrosion.



The Role of Iron Oxide in Corrosion

One consequence of iron oxide in steel-making slag is to significantly reduce the melting temperatures predicted by only considering the CaO–MgO–SiO₂ phase diagram. Some of the reaction products commonly found between basic refractories and steel-making slag are given in Table

Table 3 Reaction Products Between Steel Making Slag and Basic Refractories with Melting Points for Full Melting or Partial Melting (Peritectic Reactions)

System CaO–MgO–Al ₂ O ₃ –SiO ₂		System FeO–MgO–Al ₂ O ₃ –SiO ₂	
Mineral	Melting temperature (°C)	Mineral	Melting temperature (°C)
2MgO · SiO ₂ (forsterite)	1900	FeO · SiO ₂ (fayalite)	1205
CaO · MgO · SiO ₂ (monticellite)	1485	FeO · MgO · SiO ₂ (iron monticellite)	1230
3CaO · MgO · 2SiO ₂ (merwinite)	1575	2CaO · (Fe ₂ O ₃ , Al ₂ O ₃) · SiO ₂ (iron gehlenite)	1285
2CaO · SiO ₂ (dicalcium silicate)	2130	FeO · Al ₂ O ₃ · 5SiO ₂ (iron cordierite)	1210
3CaO · SiO ₂ (tricalcium silicate)	2070	2CaO · Fe ₂ O ₃ (dicalcium ferrite)	1489
CaO · Al ₂ O ₃ · 2SiO ₂ (anorthite)	1553	4CaO · Al ₂ O ₃ · Fe ₂ O ₃ (brownmillerite)	1395
2CaO · Al ₂ O ₃ · SiO ₂ (gehlenite)	1593	6CaO · 2Al ₂ O ₃ · Fe ₂ O ₃	1365
CaO · Al ₂ O ₃ · 2SiO ₂ and	1380		

It is immediately obvious that most of the iron-containing compounds melt in the area of 1200–1350C while most of the calcium silicate phases melt above 1485C. It is also true that melting can typically begin below these indicated temperatures by as much as 50C due to the effect of other impurities and due to the presence of multicomponent eutectics not seen on three-component diagrams. The corrosion process between calcium-iron-silicate slag and magnesiacontaining refractories can depend on the mobility and concentration of reactants.

A photomicrograph of the immediate slag–brick interface region in a brick from a steel-making furnace location above the metal line is shown in Figure 16. Here the reaction products are “mixed” iron spinel or $(\text{MgO}, \text{FeO}).(\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)$, dicalcium silicate ($2\text{CaO}.\text{SiO}_2$), and dicalcium ferrite ($2\text{CaO}.\text{Fe}_2\text{O}_3$).

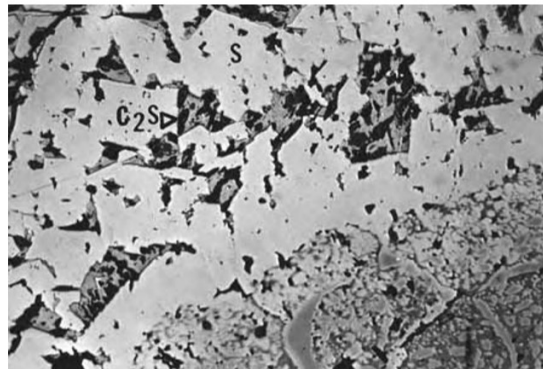


Figure 16 Corrosion interface in an MgO brick from an upper sidewall location (130×).

Because of the high concentration of iron oxide dust in the furnace atmosphere and the lack of persistent slag attack (or flow), the spinel phase formed a sort of “barrier coating” over the face of the brick. By contrast, a brick from a slag line application exhibited a very different corrosion process (Figure 17). Here the products of corrosion appear to be dicalcium ferrite ($2\text{CaO}\cdot\text{Fe}_2\text{O}_3$) penetrating around individual magnesium oxide crystals (rounded gray crystals) with isolated pockets of black-appearing dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) present in the slag layer. Magnesium oxide crystals appear to be eroded from the refractory surface in response to the extremely high temperatures and the intensity of the slag contact.

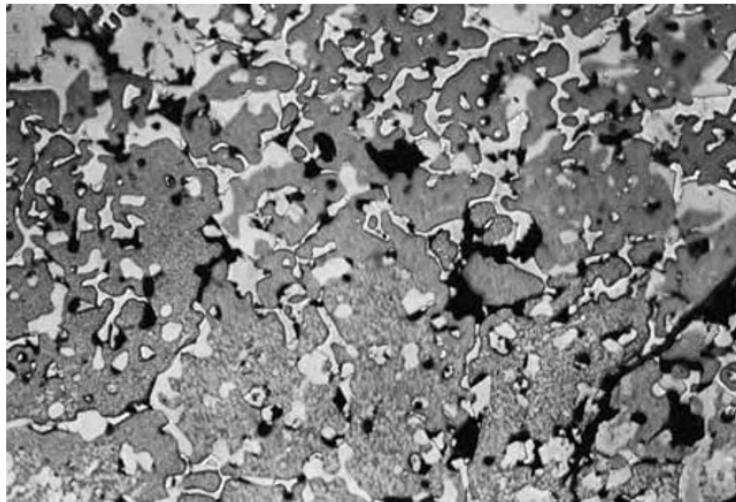


Figure 17 Corrosion interface in an MgO brick from a slag line location (130×).





Gas-Phase Reactions

The gas phase in a furnace may be the partial or even sole contributor to corrosion reactions or other deterioration in refractories. Some of the processes that have been recognized include

1. Alkali transport to refractory surfaces resulting in surface reaction and penetration
2. Reduction of the refractory and gas-phase corrosion
3. Alternating oxidation and reduction, causing sequential dimensional changes in refractories that may enhance spalling.

The potential for alkali to cause “glazing” on the surface is less well recognized than alkali compounds can volatilize in furnace atmospheres, resulting in transport of the volatile species to the surface of the refractory where vapor-phase penetration may also occur.

Table 4 Alkali Phases Found in Used Refractories

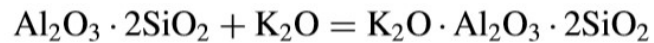
Phase	Melting Point (°C)
$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (albite)	1100
$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (carnegite)	1526
$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ (carnegite)	1220
$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ (leucite)	1686
$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (kaliophilite)	> 1700



Figure 30 Sidewall of sawdust fired tunnel kiln after seven years of service.



These oxides can cause glazing or expansion. The expansion reaction with potassium is particularly deleterious for refractories, with the reaction given as



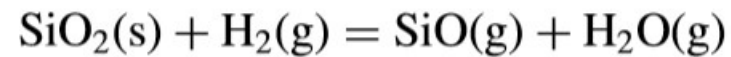
where $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ is metakaolin (a decomposition product of fireclay) and the reaction product is kaliophyllite. The volume expansion due to formation of kaliophyllite is on the order of 15% (linear expansion of 5%). As potassium is a product of combustion of sawdust, reactions of this type are expected as the cause of the problems in the sidewalls of tunnel kilns fired with sawdust and as the cause of the sheet spalling (Figure 31).



Figure 31 Crown of sawdust fired tunnel kiln after seven years showing surface glazing and sheet spalling.



Gas-phase corrosion is also known in refractories containing SiO₂. It has long been recognized that products containing SiO₂ can be “reduced” by hydrogen or by penetration of aluminum metal. The gas-phase reduction by hydrogen can be represented as;



Refractories exposed to hydrogen (or carbon monoxide) can experience gas phase removal of SiO₂ through the process of forming silicon monoxide. For example, at 1000°C, a CO/CO₂ ratio of about 1025 will be sufficient to reduce SiO₂. Mullite reduction and silica loss at temperatures exceeding 1500°C have been seen in petroleum calcining kilns.



Summary

Slag corrosion by liquids occurs whenever a threshold temperature is exceeded, which is usually when melting occurs between the refractory and the slag. Corrosion results in solution of refractory constituents in the liquid phase, resulting in loss of thickness of the refractory lining.

The rate of corrosion is dependent on the chemical environment and on the hot face temperature of the refractory. Models for the corrosion process point to the fact that hot face temperature is the most important variable in controlling refractory life.

To reduce corrosion loss, the usual approach is to employ higher-purity refractories or lower-porosity refractories (such as fusion cast brick) because precise limits on hot face temperature are not practical given process goals. In new furnace designs, consideration should be given to hot face temperature control as a strategy to attain the most economical refractory cost.

Corrosion is primarily a chemical process, and the potential for corrosion can be estimated by reference to phase equilibrium diagrams. These diagrams can allow prediction of the "threshold temperature" for liquid formation. Microscopic techniques allow identification of particular corrosion reactions. Corrosion can also take place through gas-phase reactions.

The most fundamental way to limit corrosion is to understand the chemical and physical processes involved in corrosion and to formulate strategies to minimize these processes.

5

Refractory Types

Alumina-Silica Bricks (AKA Mullite), Magnesite Refractories, Silica Brick, Dolomite Refractories



Alumina-Silica Brick

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^{-27} atmospheres—an atmosphere easily reached in a furnace packed with a form of carbon such as coke or charcoal.

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 the 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 bricks have the attributes of being relatively inexpensive—at least compared to most basic brick

Alumina-silica brick can be used in situations where modern castable refractories have disadvantages

Fire-clay bricks (low Al_2O_3) are also called-alumina silica bricks, comprise about 75% of the production of refractories on a volume basis and are essentially hydrated aluminum silicates with minor proportions of other minerals.

Alumina-silica bricks have the attributes of being relatively inexpensive—at least compared to most basic brick.

As a type they are extremely versatile; least costly of all refractory bricks and are extensively used in the iron and steel industry, non ferrous metallurgy, glass industry, pottery kilns, cement industry and by many others.

ASTM subdivides fire-clay brick into four major classifications depending primarily upon fusion temperature (Pyrometric Cone Equivalent, PCE).

The four standard classes of fireclay brick are: super duty, high-duty, medium-duty, low-duty, and also semi-silica.



Table 4 Typical Composition and Properties of Fireclay Brick

	Low-duty 1000°C max.	Medium- duty 1200°C max.	High-duty 1400°C max.	Super-duty 1600°C max.
<i>Chemical analysis</i>				
Al ₂ O ₃	25.4	29.3	37.0	41.9
SiO ₂	68.1	62.9	57.8	53.2
Fe ₂ O ₃	1.5	2.3	1.3	1.0
TiO ₂	1.5	2.9	2.3	2.2
Na ₂ O + K ₂ O	1.5	1.5	1.3	1.2
<i>Physical properties</i>				
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



These classes cover the range from approximately 18% to 44% alumina, and from about 50% to 80% silica.

Table below shows that as the quantity of impurities increases and the amount of Al_2O_3 decreases, the melting point of fireclay brick decreases.

All fire-clay brick are not alike and the total ranges of their properties are quite broad.



Table 6 Spalling Behavior of Three Fireclay Brick Brands

	Conventional	High density	Premium
<i>Chemical analysis</i>			
Al ₂ O ₃	50.8	53.2	52.9
Alkalis	1.5	1.2	1.2
<i>Physical properties</i>			
Bulk density, g/cm ³	2.18	2.34	2.34
PLC, 5 hr. @ 1480°C	0 to -0.6	0 to -1.2	-0.3 to -1
Subsidence under load %, 5 hr. @ 1450°C, 172 kPa	-3 to -5	-1.5 to -3	-1.5 to -2.5
Subsidence under load %, 100 hr. @ 1450°C, 172 kPa	-10 to -14	-6 to -10	-2 to -6
Panel spalling loss, %, 1650°C, preheat	3 to 8	2 to 6	0 to 3



Characteristically, fire-clay brick begin to soften far below their fusion temperature and under load actual deformation takes place.

The amount of deformation depends upon the load, and, once started, this deformation is a slow but continuous process unless either the load or the temperature is reduced.

It is for this reason that fire-clay brick are not well adapted for use in wide sprung arches in furnaces operating continuously at high temperatures.



High Alumina Refractories

Alumina refractory which consists of aluminum oxide and traces of other materials is the most mature of the engineering ceramics.

Alumina is one of the most chemically stable oxides known, which offers excellent hardness, strength and spalling resistance.

It is insoluble in water and super heated steam, and in most inorganic acids and alkalis.

Alumina refractories carry the all purpose characteristics of fireclay brick into higher temperature ranges that makes it suitable for lining furnace operating up to 1845°C.

It has a high resistance in oxidizing and reducing atmosphere and is extensively used in heat processing industries.

The refractoriness of high alumina refractories increases with increase of alumina percentage.

The 50%, 60%, 70% and 80% alumina classes contain their respective alumina contents with an allowable range of plus or minus 2.5%.



High-alumina brick are classified by their alumina content according to the following ASTM convention. These are:

Mullite refractory: Mullite brick is about 72wt% alumina with 28wt% silica. These have excellent volume stability and strength at high temperatures.

Corundum refractories: The 99% alumina class of refractories is called corundum. These refractories comprise single phase, polycrystalline, and alpha-alumina.

High alumina bricks are most commonly used in cement, lime and ceramic kilns, glass tanks, crucibles for melting a wide range of metals, hearth & shaft of blast furnaces and in lead dropping furnaces.

1. One compound known as mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) 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°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.

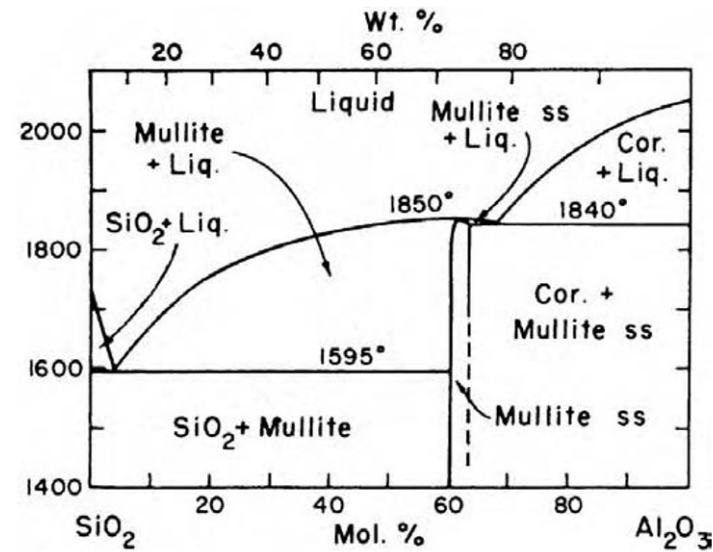


Figure 1 The alumina-silica phase equilibrium diagram. (From Ref. 2.)

2. The diagram has a “solidus” line at 1595°C, meaning that compositions ranging from just below 100% SiO₂ (0% Al₂O₃) to the mullite composition (60 mole % Al₂O₃ or 72 weight % Al₂O₃) exhibit solid phases (for example, cristobalite—a form of SiO₂—or glass and mullite) unless the temperature exceeds 1595°C (the binary eutectic temperature between SiO₂ and mullite). The term “glass” signifies the presence of a vitreous and noncrystalline phase. It can be present along with a small percentage of “free” or uncombined crystalline silica. Above 1595°C, a refractory in this composition range would be obviously useless as it would be partially liquid phase or melted (denoted as “Liq.” in Figure 1).

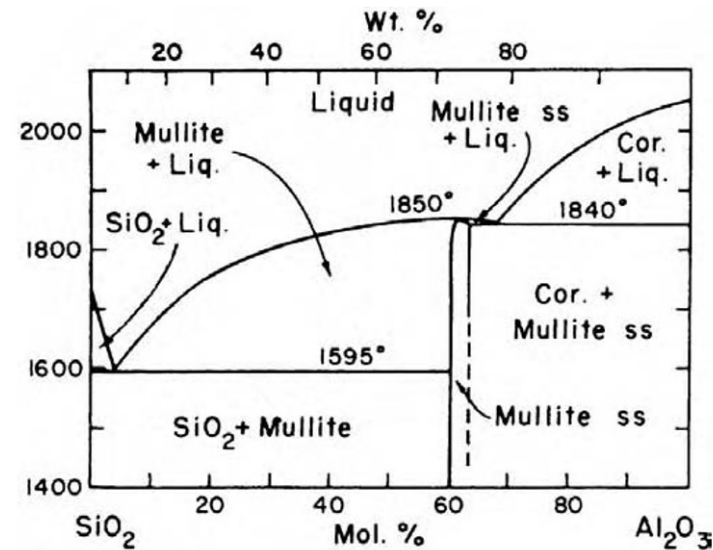


Figure 1 The alumina-silica phase equilibrium diagram. (From Ref. 2.)

3. 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 “Cor.” in Figure 1) has a melting point of about 2050°C.

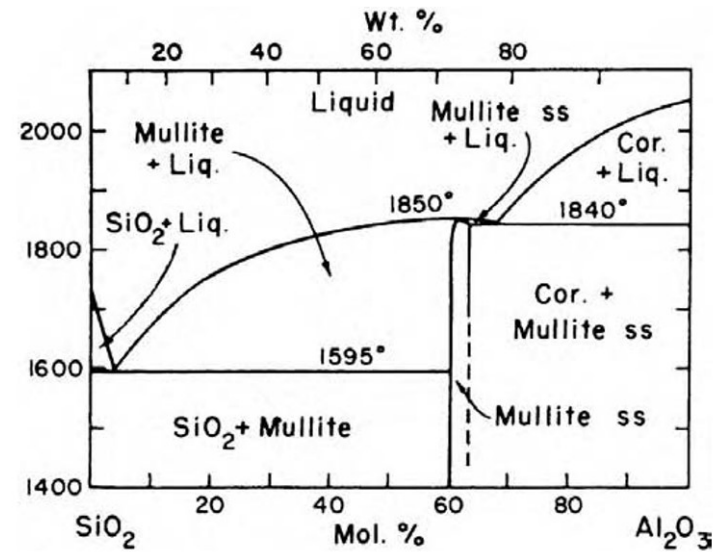


Figure 1 The alumina-silica phase equilibrium diagram. (From Ref. 2.)



The Al_2O_3 - SiO_2 phase diagram can be used to explain the “classes” of alumina-silica brick in terms of generalized “refractoriness.” These classes are given in Table 1 along with comments on the 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.

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 <i>Phases</i>	General performance <i>in the absence of slag corrosion or alkali attack conditions</i>
Less than 50% Al_2O_3	Fireclay (Chamotte) <i>Phases on phase diagram:</i> mullite and glass (can contain "free SiO_2 ")	Usually made from 100% fireclay Highest-quality grades usable to about 1600°C ("super-duty" 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 <i>Phases on phase diagram:</i> 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 in excess of 1700°C
70% Al_2O_3	Mullite <i>Phases on phase diagram:</i> 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 <i>Phases on phase diagram:</i> 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 <i>Phases on phase diagram:</i> 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



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 the press for subsequent drying and firing

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

Information	Fireclay (calcined basis)	Andalusite	Calcined refractory bauxite (Guyana)	Tabular alumina
Usual calcination temperature, °C	Can be used as calcined aggregate (1450°C+) or as raw clay	Not calcined	1450°C	>1750°C
Chemical analysis, %				
Al ₂ O ₃	39.7	61.3	88.7	99.5
SiO ₂	54.0	37.4	6.5	<0.1
TiO ₂	2.80	0.25	2.84	Tr.
Fe ₂ O 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 ₂ O	0.20	0.08	Tr.	0.25
K ₂ O	0.60	0.06	Tr.	Tr.
LOI	0.15	0.13	0.05	0.04



Production

The best alumina-silica bricks 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 be free of opportunities for contamination by inadvertent mixing of lower-quality raw materials with higherquality 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 1970s.

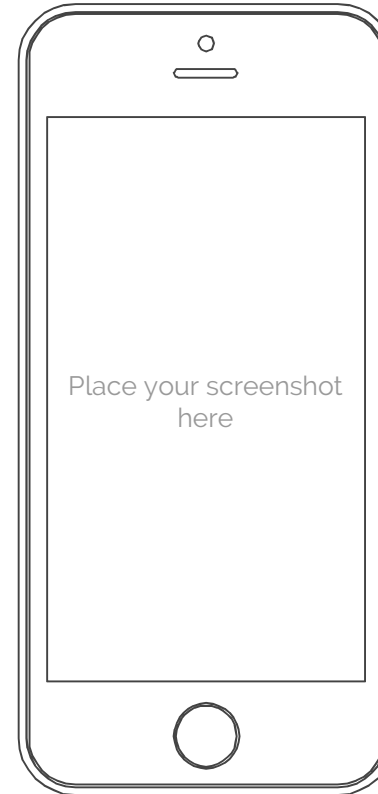
Conveyance—Are conveyors covered to prevent contamination? If bucket elevators are used, is the manufacturer trying to prevent particle size segregation?

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?

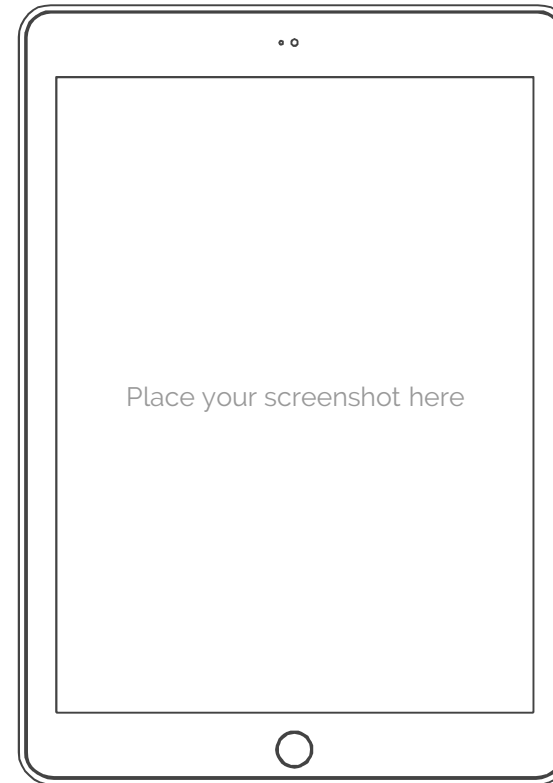
iPhone Slides

Lecture notes available



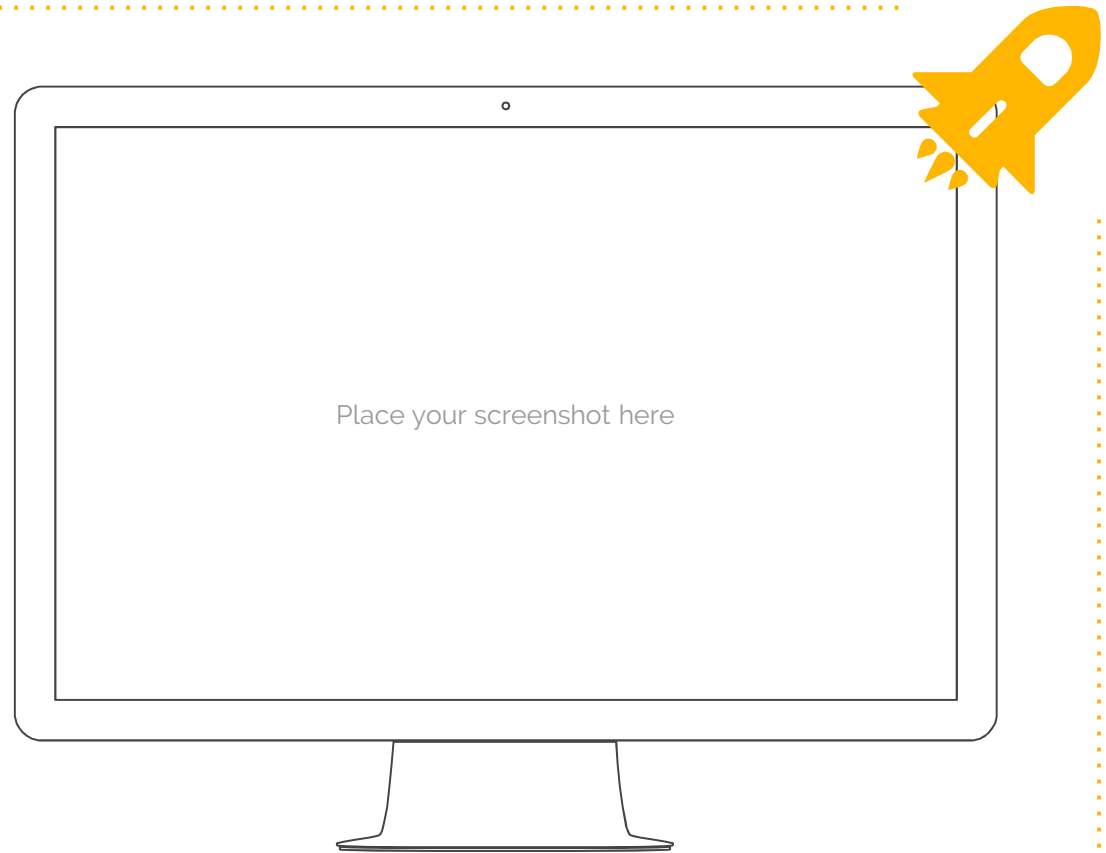
Tablet Slides

Lecture notes available



Desktop Slides

Lecture notes available





Thanks!

Any questions?

You can write! bcicek@yildiz.edu.tr