

A Comprehensive Review on Refractory Materials for Furnaces and Reactors: Selection, Preparation, Performance and Life-Cycle Engineering

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ABSTRACT

Refractory materials are essential for both high- and low-temperature industrial processes because they provide thermal insulation, structural strength, protection between hot working environments and furnace shells. The present paper reviews common refractory types such as alumino-silicate, alumina, magnesia, zirconia, silicon carbide and carbon-based materials, including both brick and monolithic forms. Their thermal, mechanical and chemical behaviour is discussed in relation to various furnaces, reactors used in steel, iron, cement, glass, non-ferrous, and petrochemical industries. The study explains the main causes of refractory damage, including slag corrosion, chemical attack (alkali, chloride, sulphate), carburization, oxidation, infiltration, thermal shock, creep and mechanical wear. These degradation mechanisms are linked with practical strategies for design, material selection and operation. A multi-criteria framework is presented to help select linings based on service conditions such as temperature, atmosphere, slag chemistry, thermal cycling and maintenance requirements. Case studies on electric arc furnaces, cement rotary kilns and steam methane reformers show the trade-offs between bricks and monolithic. Finally, methods for testing, monitoring, life assessment and maintenance practices are outlined to improve refractory reliability and reduce overall costs.

Keywords: Refractory, Alumina, Magnesia, Alumino-silicate, Carbon-refractory, Monolithic

1. INTRODUCTION

The materials which are used in industries to withstand high temperatures, such as steelmaking, cement, petrochemicals and non-ferrous metallurgy are known as **Refractory Materials**. Furnaces and reactors in these industries face extreme heat, chemical attack and mechanical stress. To handle these conditions, materials are needed that can stay strong, resist damage and keep their properties at very high temperatures. Refractories, which are usually made from oxides like alumina, silica, magnesia, and zirconia, are essential for keeping furnaces and reactors efficient, saving energy and lasting longer. Instead of this, carbide, nitride and sulphide-based refractories are also used. Over the years, material science has developed new types of refractories with improved properties to meet modern industrial needs.

However, many challenges still exist regarding the failure mechanism. Refractory failure is one of the main causes for unexpected furnace or reactor shutdown resulting in high costs and production losses. Problems such as cracking due to heat (thermal spalling), corrosion from slags, chemical penetration and mechanical wear reduce the life of refractory linings. In addition, industries now focus on sustainability and energy efficiency, which requires refractories that not only survive harsh conditions but also save energy, improve performance, and reduce environmental impact. To solve these issues, it is important to clearly understand refractory properties, how they are selected, and how they behave in real working conditions.

The study executes connection of material science with industrial applications, providing a gateway to obtain sustainable refractory solutions for modern furnaces and reactors.

2. Refractory Materials for Furnace and Reactor

Refractory materials are absolutely essential for both high-temperature and low-temperature industrial processes across sectors like steel, iron, cement, glass, non-ferrous metallurgy and petrochemicals, fundamentally serving to provide thermal insulation, structural strength and vital protection between the extreme hot working environments and the external furnace or reactor shells [1]. These materials, which are generally ceramics composed of oxides such as alumina (Al_2O_3), silica (SiO_2), magnesia (MgO) and zirconia (ZrO_2) or non-oxides like silicon carbide (SiC) and carbon are engineered to retain their strength and properties while facing extreme heat, chemical attack, and mechanical stresses [2]. Their utility mandates a careful classification based on chemical behaviour, which is critical for material selection for instance, **acidic refractories**, like those rich in SiO_2 or aluminosilicates are stable in acidic process environments but are highly vulnerable to corrosion by basic slags, while **basic refractories**, primarily composed of MgO and CaO (doloma), thrive in basic environments but are prone to attack by acidic substances [3]. Bridging this gap are **neutral refractories** such as alumina, chromia and carbon, which are chemically inert and versatile, showing resistance to both acidic and basic media [4]. Further categorization by raw material reveals specialized families, including **high-alumina refractories** (50% to over 90% Al_2O_3) which offer high refractoriness and spalling resistance and **silica refractories** (at least 93% SiO_2) known for their resistance to acidic slags, abrasion and their unique ability to withstand heavy loads without softening until their fusion point is nearly reached, making them indispensable in applications like glass-melting furnace superstructures [5]. **Zirconia refractories** are crucial for ultra-high temperature use ($\geq 1900^\circ\text{C}$) in areas like casting nozzles and crucibles, valued for their very low thermal conductivity, which provides excellent high-temperature insulation and minimal reaction with liquid metals [6]. In terms of physical form, the lining may consist of traditional **shaped refractories** (bricks/tiles), which are factory-processed for consistent density and dimensional tolerances, making them the preferred choice for zones requiring precise geometry or exceptional mechanical wear resistance [7]. Alternatively, **unshaped** or **monolithic refractories** (castables, gunning mixes, ramming masses) are shaped **in-situ**, producing nearly joint-free linings that conform to complex geometries, allow rapid repair and are becoming common substitutes for bricks due to their tunable properties and ease of installation [8]. Despite continuous improvements in material science, refractory linings face numerous challenges in service, as their failure is a major cause of unexpected furnace or reactor shutdowns leading to significant production losses and costs [9]. The primary degradation mechanisms include **chemical attack** from molten metal and slags

(corrosion), **thermal shock** which leads to cracking and spalling, and mechanical phenomena such as creep and wear [10]. Therefore, modern refractory engineering focuses on a multi-criteria selection framework that considers not just the operating temperature and loads, but also the specific atmosphere, slag chemistry and thermal cycling frequency. To meet these demanding conditions, **composite and functional refractories** have emerged, such as magnesia-carbon (MgO-C) and alumina-silicon carbide-carbon (Al₂O₃-SiC-C) systems, which combine multiple phases to provide superior corrosion resistance, high thermal shock resistance and enhanced mechanical strength [12]. Contemporary industry efforts also strongly emphasize **sustainability** and **energy efficiency**, driving the need for refractories that reduce environmental impact and save energy [13], which is supported by a documented progression toward high-density, low-porosity monolithics and optimized composite chemistries that have shown marked performance improvements in terms of thermal-shock cycles and slag-corrosion resistance over conventional fired units [14]. The lifecycle engineering of these vital industrial components is thus a continuous balance between maximizing durability through engineered microstructures, ensuring high-temperature stability and minimizing operating costs.

3. Classification and Properties of Refractories

Brief classification of Refractory Materials

Below the refractories are classified based on the different parameters like, chemical behaviour, chemistry, shape, function and specialized.

By chemical behaviour / composition

- **Acidic Refractories-** the Acid Refractory are a kind of lining material rich in SiO₂ / alumino-silicates (e.g., silica, fireclay). Stable in acidic environments but easily corroded by basic materials. They are mainly used where slags/processes are acidic. [1]
- **Basic Refractories-** the Basic Refractory are a kind of refractory rich in MgO, CaO (e.g., magnesia, doloma, magnesia-carbon). Stable in basic environments but easily corroded by acidic materials while suited to basic slags/environments. [1]
- **Neutral Refractories-** Chemically inert to both acidic and basic environments; versatile and stable. Alumina (Al₂O₃), chromia (Cr₂O₃), Carbon (graphite), Chromite, etc.; tolerant to both acidic and basic media. [1]

By main raw-material / chemistry (common families)

- **Alumina-based** (high-Al₂O₃, tabular alumina, bauxite) - **High-Alumina Refractories** Contain at least 50% Al₂O₃; can go up to 90 % or more. As the alumina content increases, so does refractoriness and resistance to heat and spalling.[1]
Extra-High Alumina Refractories defined as having 87.5-100% Al₂O₃; highly dense and stable at very high temperatures (~1,800 °C and above) [2]
- **Silica (SiO₂)-** Silica refractories, composed primarily of **Silicon Oxide (SiO₂)** with at least 93% purity, are manufactured from quartzites, fused silica, or silica gravel with

low alumina and alkali contents, and are often chemically bonded with 3-3.5% lime. They exhibit excellent resistance to acidic slags, abrasion, flux, and slag corrosion, while maintaining volume stability and high spalling resistance. A key property is their ability to **withstand heavy loads without softening** until their fusion point (**1713°C**) is nearly reached, making them highly durable at elevated temperatures. Various grades exist, such as **coke-oven quality**, **conventional**, and **super-duty** and characterized by very low impurity content, widely used in the **superstructures of glass-melting furnaces**. Additionally, their high refractoriness and superior resistance to thermal shock make silica refractories **indispensable** in iron and steel industry furnaces and other high-temperature applications. [1] [2]

- **Magnesia (MgO) / Dolomite**- The main constituent of these refractories is **magnesia (MgO)**. The main sources of magnesia are brines and seawater as well as sintered and fused magnesia. Magnesia- carbon refractories are important refractories of this type. [1]
- **Zirconia (ZrO₂) and special oxides**- In **zirconia refractories**, main constituent of the refractory is zirconium oxide (ZrO₂). Zirconia refractories are useful as high temperature construction materials. They tend to be used in applications where temperatures are **above 1900°C** such as **casting nozzles and gates, crucibles, furnace liners and kilns**. The thermal conductivity of zirconium dioxide is found to be much lower than that of most other refractories and the material is therefore used as a high temperature insulating refractory. Since Zirconia shows **very low thermal losses** and does not react readily with liquid metals, it is mainly useful for making **refractory crucibles and other vessels** for metallurgical purposes. [1]
- **Non-oxide / carbon & SiC**- The main constituent for these refractories is carbon. Carbon, formed carbon, manufactured carbon, amorphous carbon and baked carbon are the terms which are used for these refractories. Carbon can also be in graphitized or semi-graphitized form. The carbon refractories are primarily used in highly reducing environments. Carbon refractories have a high refractoriness and high temperature of softening under load. They resist well the action of slags and have high thermal stability. Silicon carbide (SiC), graphite, C-containing bricks (MgO-C, Al₂O₃-C) for conductive/erosion-resistant linings. [1]

By product form / shape

- **Shaped refractories (bricks/tiles)**- Shaped refractories are the traditional preformed products - bricks, tiles, speciality shapes and crucibles - that are manufactured in factories to a fixed geometry, fired (or otherwise processed) and then delivered ready to install. Because they are produced under controlled conditions they offer consistent density, composition and dimensional tolerances, which makes them easy to design into repeatable lining patterns, to inspect by standard non-destructive tests, and to predict performance in service; shaped products are commonly made from fireclay, high-alumina, magnesia, silicon carbide or other engineered mixes depending on the furnace chemistry, and they remain the preferred choice where precise geometry, high abrasion resistance and well-known service behaviour are needed. [3]

- **Unshaped / monolithic refractories-** Unshaped or monolithic refractories are supplied as powders, mortars or plastic masses that are given their shape in place during installation (by casting, gunning, ramming, or trowelling) and then cured or dried in situ; this approach produces nearly joint-free linings that conform to complex geometries, reduces the energy and cost associated with factory firing, and enables rapid repair and graded or layered lining architectures. Modern research and industry reviews emphasise that monolithic which include castable, ramming masses, gunning mixes, mortars and dry vibratable products are highly tunable through binder choice, particle grading and additives, allowing engineers to balance strength, thermal shock resistance, slag resistance and installation speed, so monolithics are increasingly chosen as substitutes for shaped bricks in many applications while still relying on shaped units for zones requiring exact shapes or exceptional mechanical wear resistance. [4]

By performance / function

- **Insulating refractories-** Insulating refractories are mainly used to reduce heat loss and control temperature in furnaces and reactors. They are placed behind the main working lining or in areas where heavy mechanical loads are not present, such as furnace roofs or doors. These refractories are made of highly porous ceramics like mullite, silica, or lightweight alumina- and magnesia-based materials. Their porous structure, often created by additives like foam or fibres, helps trap air and lower thermal conductivity. This makes them lightweight and efficient at insulation, but at the same time lowers their strength and makes them more prone to damage or infiltration by molten metal and slags. Their performance is judged by their ability to stay strong under heat, resist thermal shock during temperature changes, and maintain low thermal conductivity over time. Researchers like Rafael Salomão and colleagues have shown how processing methods such as pore-forming agents or even 3D printing can improve their performance for high-temperature [5]
- **Dense / load-bearing refractories-** Load-bearing or structural refractories, on the other hand, are used directly in contact with molten metals, slags, and flames. These refractories form the working lining of furnaces, ladles, and converters, and must withstand both high mechanical loads and chemical attack. They are often made from dense materials such as high-alumina, magnesia, alumina-magnesia spinel, or carbon-containing systems like MgO-C and Al₂O-C. Their performance depends on high strength at service temperature, resistance to thermal shock, and their ability to resist corrosion and slag penetration. Failures usually occur due to chemical dissolution by slags, penetration into open pores, thermal cracking, or oxidation of carbon in carbon-based refractories. To measure performance, tests such as crushing strength, thermal shock, and slag penetration are used, often combined with thermodynamic modelling. Reviews by Sarkar and Sohn provide detailed explanations of how alumina and magnesia refractories interact with slags, while Tang and other colleagues have studied how additives like calcium-magnesium-aluminate improve the performance of alumina-magnesia mixes.
- **Chemical-resistant / anti-corrosive refractories-** Chemical-resistant refractories are tailored to resist attack from very corrosive environments such as molten glass,

molten aluminium alloys, or highly basic slags. Their role is less about mechanical strength and more about surviving chemical dissolution and reaction. For example, zirconia-rich fused cast refractories are used in the glass industry because they are very resistant to corrosion. Magnesia and magnesia–chromite refractories are common in steelmaking for resisting basic slags, while nitride ceramics like AlN, Si₃N₄, and BN are employed in contact with aggressive non-ferrous melts. To improve resistance, researchers often add special non-wetting agents such as BN, BaSO₄ (Barium Sulphate), or CaF₂ to reduce penetration, or apply coatings. Failures usually happen due to dissolution, penetration, or chemical reactions that create new phases like spinel, which can weaken the structure. Their performance is often tested by immersion in molten metals, contact angle measurements, or long-term pilot trials. A short review by Barandehfard and colleagues focuses on improving aluminosilicate refractories for molten aluminium alloys with non-wetting additives, while other papers cover corrosion in magnesia-based refractories and zirconia-rich refractories for the glass industry.

By specialized / advanced classes

- **Fused-cast refractories** (e.g., fused silica, fused alumina) -Fused-cast refractories are special glassy-ceramic blocks made by melting raw materials such as alumina–zirconia–silica (AZS), high-zirconia, or high-alumina mixtures, and then cooling them in a controlled way. This process creates a very dense, smooth and low-porosity structure with both glassy and crystalline phases. They are designed for the most demanding parts of glass furnaces, such as tanks and forehearth, because their compact surface resists chemical attack, wetting and penetration by molten glass much better than ordinary sintered bricks.

Under the microscope, fused-cast blocks show a mix of a glassy phase and tiny crystals. In AZS refractories, these crystals are mainly zircon, zirconia, and alumina. Research shows that the behaviour of the glassy phase such as how easily it softens, melts, or contains impurities has a bigger impact on performance than bulk properties like overall density or zirconia content.

Since the glassy phase can sometimes soften or leak out under high furnace temperatures, manufacturers carefully control the melting and solidification process, the atmosphere used during casting (oxidizing or reducing), and impurity levels. They also rely on advanced testing methods like ultrasonics and imaging to check quality and ensure reliability.

In practice, fused-cast AZS is still the most widely used material when high glass quality and long service life are needed. High-zirconia or high-alumina fused products are used in special furnace zones. Recent studies focus on understanding the glassy phase better and improving non-destructive testing methods to increase furnace performance and durability. [6]

- **Composite and functional refractories-** Composite refractories are a group of specially designed materials made by combining two or more different phases so the final product performs better than any single material alone. In industry, this often means carbon-containing refractories like alumina-carbon (Al₂O₃-C) or magnesia–

carbon (MgO-C), where carbon (in forms such as graphite, coke, or carbon black) is mixed into an oxide base. The carbon helps resist thermal shock, improves heat transfer, and prevents molten metal from sticking, while the oxide provides strength and chemical resistance.

The term also includes newer ceramic-matrix composites (CMCs) and refractories reinforced with short fibres or particles. These are developed to reduce brittleness, improve toughness, control expansion at high temperature, and adjust corrosion resistance. Recent research has looked at optimizing the type, size, and distribution of these added phases-ranging from nano-carbons and silicon carbide fibres to oxide whiskers. Work is also being done on low-carbon versions for cleaner steelmaking, and on nanoscale additives that control grain growth, porosity, and bonding between phases to extend service life.

Studies show that additives, antioxidants, layered structures, and new processing techniques such as binder pyrolysis, infiltration, or even 3D printing can improve oxidation resistance, reduce carbon loss, limit slag attack, and boost thermal shock resistance. A growing trend is the use of “functionally graded” or fibre-reinforced composites, where different layers or reinforcements are tailored for extreme furnace conditions.

In short, composite refractories are designed to balance tough but sometimes conflicting needs like high toughness, strong chemical resistance, and low carbon pick up. Modern research focuses on both understanding how they work at the microscale and scaling up these designs for steel, non-ferrous, and glass industries.[7]

4. Properties of Refractory Materials

Here the properties (like thermal, mechanical, chemical and electrical properties) of the different refractory materials which have been mentioned in brief of different categories in terms of chemistry:

Acidic refractories-Acid refractories (like, Silica and Alumino-Silicate) display unique thermal behaviour due to quartz-to-tridymite transformations causing predictable volume changes between 500-900°C. Once converted, they offer low thermal expansion and good thermal shock resistance within their operating range. Mechanically, they provide strong load-bearing capacity at high temperatures in oxidizing or acidic atmospheres, with good cold crushing strength, though they are prone to spalling during rapid heating through phase changes. Chemically, they excel in resisting acidic slags and atmospheres but are severely attacked by basic oxides and slags, requiring careful selection for mixed environments. Electrically, they act as high-resistivity insulators unless modified with conductive phases. [8]

Basic refractories -Basic refractories, such as magnesia-based materials, are characterized by very high refractoriness and relatively high thermal conductivity, which facilitates heat transfer but can increase lining temperatures in certain designs. Mechanically, they possess excellent hot strength and abrasion resistance under steelmaking conditions, though their performance depends on factors like densification,

bonding methods and impurity levels, which influence creep resistance. Chemically, they are specifically engineered to withstand basic slags rich in CaO and MgO, making them ideal for converters, BOFs, and ladles, but they are vulnerable to acidic slags and silica-rich melts. Electrically, they act as insulators unless modified with carbon or SiC.[9][10]

Neutral refractories-Neutral refractories exhibit good refractoriness with stable thermal performance across a wide temperature range, offering intermediate thermal conductivity between insulating and highly conductive materials. Mechanically, they provide strong hot-load capacity and superior creep resistance compared to many acidic bricks, with chromia additions further enhancing slag-wetting resistance in certain compositions. Chemically, they are termed “neutral” as they withstand both acidic and basic slags, making them suitable for environments with mixed chemistry; however, chromia use involves environmental and regulatory concerns. Electrically, they function as insulators unless conductive phases like carbon or silicon carbide are incorporated to modify their properties. [1][11]

Alumina-based refractories - Alumina (Al_2O_3) refractories offer high refractoriness and thermal stability, with thermal conductivity influenced by density and phase tabular and fused alumina showing superior high-temperature strength and conductivity compared to lower grades. Mechanically, they demonstrate excellent cold crushing strength, high modulus of rupture at elevated temperatures, and good creep resistance when properly formulated. Chemically, alumina is largely inert to slags and molten metals, though corrosion resistance depends on slag composition, with acidic and basic slags affecting it differently. Electrically, alumina functions as an excellent insulator across most service ranges, with conductivity increasing only under extreme conditions or with conductive doping. [1][2][12]

Silica-based refractories –Silica based refractories exhibit distinct thermal, mechanical, chemical, and electrical characteristics. Thermally, they undergo quartz-to-cristobalite transformations, producing step changes in expansion that are managed through pre-conversion or controlled heating, resulting in stable, low-expansion linings. Mechanically, they offer high compressive strength at service temperatures, making them suitable for applications like glass tank crowns and coke ovens. Chemically, they show excellent resistance to acidic melts and oxidizing atmospheres but are highly vulnerable to basic slags. Electrically, they function as strong insulators, maintaining high resistivity unless intentionally modified with conductive phases. [1][2][13]

Magnesia (MgO) / Dolomite-based refractories - Dolomite-based refractories are valued for their high refractoriness and low thermal conductivity, with performance strongly influenced by impurity levels and the extent of sintering or fusion. Mechanically, they offer strong hot strength, abrasion resistance, and dimensional stability in basic-service conditions, making them well-suited for applications like converter hearths and ladles, dolomite is particularly effective where limited sintering at service temperatures is acceptable. Chemically, they provide excellent resistance to basic slags and highly alkaline environments but are easily attacked by acidic slags and siliceous agents.

Electrically, they behave as oxide ceramics with low electronic conductivity, allowing ionic conduction only at elevated temperatures. [9][10]

Zirconia-based refractories - Under ambient pressure, pure zirconia is monoclinic up to about 1170°C, transforms to tetragonal between 1170 to 2370°C, and becomes cubic above 2370°C to its melting point. Grain size, particle shape, stabilizing oxides, and interactions with other phases influence these transformations and their metastability. Zirconia frameworks exhibit mechanical strengths up to three times higher than other all-ceramic materials and can endure physiological posterior forces, though connector regions remain fracture-prone, making their dimensions critical. Chemically, zirconia is highly inert and resists corrosive melts, serving in glass-contact and wear applications. While insulating at room temperature, doped zirconia conducts oxygen ions at elevated temperatures. [14]

Non-oxide refractories (carbides/nitrides/borides) - Non oxide materials (like, SiC and SiN etc.) are excellent candidates for high-performance applications due to their outstanding thermos-mechanical properties and their strong corrosion resistance. SiC materials can be processed in various forms, from nanomaterials to continuous fibers. Common applications of SiC materials include the aerospace and nuclear fields, where the material is used in severely oxidative environment. Very hard & abrasion-resistant and fracture toughness property of non-oxide materials. In oxidizing environments these materials form protective silica scales (SiO₂) that can protect from the oxidising environment. Chemical compatibility with the service medium must be checked carefully. Many non-oxide refractoriness are semiconducting or electrically conductive. Graphite and other carbonaceous phases yield significant electrical conductivity that rises with temperature. [15]

Shaped refractories (bricks/shapes) - Shaped refractory products, such as dense fired bricks, possess relatively larger and more uniform pores, typically around 20 to 25 microns, and in special grades about 5 microns. Their structure is stable, giving them good dimensional consistency at high temperatures. Unlike monolithic castables, they do not rely on on-site mixing or curing, so they avoid installation-related problems and variability. They offer reliable strength without the characteristic strength drop seen in castables at intermediate temperatures. Their behaviour under heat is more predictable because their ceramic bonds are already fully developed before use. However, shaped refractories generally have higher thermal conductivity and lower thermal shock resistance compared to microporous castables.[16]

Unshaped / monolithic refractories (castables, gunning/ramming mixes) - Unshaped or monolithic refractories such as Al₂O₃-SiC-C and Al₂O₃-C castables exhibit high purity, low porosity, and a characteristic microporous structure, formed through controlled particle size distribution and the use of ultrafine or nano-sized additives. This fine pore structure typically results in medium pore diameters of only 1-2 μm, providing enhanced strength, excellent thermal shock resistance, and reduced thermal conductivity compared to shaped bricks. The presence of SiC and carbon further improves slag and metal corrosion resistance, while also aiding crack resistance. Use of SiO₂-sol binders

prevents the formation of low-melting phases by eliminating lime, improving high-temperature stability. Organic fibers assist in drying and densification, minimizing cracking during heating. Monolithics also possess good deformability, allowing them to relieve thermal and mechanical stresses during service. [17]

Constituent	WTA	Calcined Al ₂ O ₃	Reactive Al ₂ O ₃	Microfine SiO ₂	SiC	Sillimanite sand	Floke graphite	SiO ₂ -sol
SiO ₂	0.04	0.2	0.03	98.6		37.10		39.8
Al ₂ O ₃	99.4	98.0	>99.5			61.66		
Fe ₂ O ₃	0.04	0.06	0.03			0.28		
TiO ₂		0.11						
CaO								
MgO								
Na ₂ O	0.14	0.3	0.07	0.06		0.58		
K ₂ O	0.02	0.04						
LOI		0.2		0.42				59.5
SiC					98			
C							98.5	
Average size		6-8	>99% <45 μm	>99% <45 μm	>98% <90 μm	>98% <250 μm	D ₅₀ = 43.2	~14 nm
Bulk density (g/cm ³)	3.61							
Apparent porosity (%)	3.92							

Characteristics of organic fiber: length, 5 mm; density, 0.9 g/cm³; average diameter, 50 μm; tensile strength, 300-400 MPa.

Figure 1: Physical and Chemical Properties of Raw Materials [17]

However, they require careful on-site mixing, installation, and controlled drying. Conventional hydraulically bonded castables may show temporary strength reduction within intermediate temperatures (250 to 600 °C), and some dimensional instability can occur at high temperatures due to matrix shrinkage. [16][17]

Insulating refractories - The desirable feature of insulating bricks is the low thermal conductivity, which usually results from a high degree of porosity. Structure of air insulating material consists of minute pores filled with air, which have very low thermal conductivity. The air spaces inside the brick prevent the heat from being conducted but the solid particles of which the brick is made conduct the heat. So, in order to have the required insulation property in a brick, a balance has to be struck between the proportion of its solid particles and air spaces. The thermal conductivity is lower if the volume of air space is larger. Importantly, the thermal conductivity of a brick does not so much depend on the size of pores as on the uniformity of size and even distribution of these pores. Hence, uniformly small sized pores distributed evenly in the whole body of the insulating brick are preferred. [18]

Dense / load-bearing refractories -Tabular alumina is the dominant synthetic high purity Al₂O₃ aggregate for high-performance refractories due to its superior refractoriness, thermal shock resistance, creep resistance, and abrasion resistance¹. It's a homogeneously sintered dense aggregate with a high

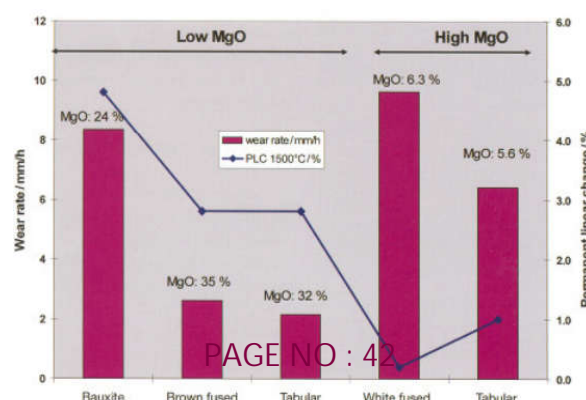


Figure 2: Slag resistance of Alu-Mag-Carbon bricks [19]

melting point of 2050°C. Its microstructure features small, spherical closed pores, which act as crack stoppers and contribute to its high thermal spalling resistance (TSR).

Micro-structural feature results in high crushing strength even after thermal shock. Tabular alumina also offers consistent properties due to its continuous sintering process. Compared to White Fused Alumina (WFA), tabular alumina yields bricks with higher bulk density, lower apparent porosity, and outstanding cold and hot strength. Tabular alumina-based bricks also show the highest abrasion resistance and outperform WFA bricks in corrosion and infiltration resistance against slags. [19]

Chemical-resistant/anti-corrosive refractories -Refractories must exhibit excellent resistance to chemical attack, enduring exposure to molten metal, ferruginous slag, and flue gases at high temperatures. The indigenous kaolinitic clay studied contained high levels of impurity oxides (approx. 8%), including Na₂O, CaO, and K₂O. These oxides are deleterious as they act as fluxing agents, reducing the fusion temperature and facilitating a liquid phase at high heat. The natural clay also showed a pronounced colour change due to iron oxide, which is often an indicator of impurities.

The synthetic alumina/silica blend was engineered to be devoid of these harmful impurities. This purity resulted in improved properties, such as no colour variation across firing conditions and a very low linear shrinkage range (0-4%), suggesting low strain of expansion and contraction. Overall, the synthetic blend exhibits refractory properties that approximate standard alumina-silicates. [20]

Fused-cast refractories (e.g., AZS, fused alumina)- Fused cast AZS (Al₂O₃-ZrO₂-SiO₂) refractories are widely used in glass-melting furnaces due to their high corrosion resistance and dense microstructure. Their structure consists mainly of monoclinic ZrO₂ and α-Al₂O₃, embedded within a residual glassy phase. Two forms of ZrO₂ occur: large compact crystals (50-200 μm) and dendritic crystals; both originate from tetragonal ZrO₂ formed during cooling, which later transforms to monoclinic structure. The glassy phase also contains very fine tetragonal ZrO₂ nanoparticles (a few nm to ~ 130 nm), stabilized by small additions of Y₂O₃ (Yttrium Oxide) and similar impurities, preventing their phase transformation during cooling. The absence of interconnected pores and the dense microstructure contribute to excellent corrosion resistance against molten glass and reduced penetration. Mullite may form only after long-term thermal exposure or reheating, depending on composition and thermal history.[21]

Composite & functional refractories (e.g., MgO-C, Al₂O₃-C, Al₂O₃-SiC-C, ZrO₂-toughened) - Composite and functional refractories are designed to combine multiple phases and roles to meet demanding steelmaking conditions. Composite refractories, such as MgO-C, Al₂O₃-C, and SiC-containing materials, provide high corrosion resistance, thermal shock resistance, and mechanical strength by integrating carbon and ceramic phases. Functional refractories include slide gate plates, submerged entry nozzles and gas purging plugs, which require controlled porosity and oxidation resistance to perform tasks like flow control, gas stirring, and preventing steel re-oxidation. These materials must withstand rapid heating, slag attack, erosion, and thermal cycling while maintaining

dimensional stability. Advances focus on improving durability, minimizing carbon oxidation, developing cleaner bonding systems, and enhancing performance through engineered microstructures.[22]

5. Assessment of the Performance of the Refractories under the thermal, chemical and mechanical stresses:

The diverse classes of refractories described above exhibit different behaviors when exposed simultaneously to thermal, chemical, and mechanical stresses and their performance can be assessed by examining composition and microstructure relationship which dictates resistance to heat, corrosion, and load:

Acidic refractories such as silica and aluminosilicates exploit the quartz-to-tridymite/cristobalite transformations to achieve low expansion and good thermal-shock resistance once converted, so they maintain dimensional stability and strong load-bearing capacity in oxidizing or acidic atmospheres. However, the same phase changes that provide stability after conversion can cause spalling if the temperature ramp is uncontrolled, and their chemical inertness collapses in contact with basic slags where rapid fluxing and structural degradation occur. [08][13]

Basic refractories like magnesia and dolomite are almost the chemical inverse, combining very high refractoriness and thermal conductivity with excellent hot strength and abrasion resistance, making them ideal for BOF linings or ladles handling lime-rich slags. However, they can be attacked by silica, so they need protection from acidic vapours or mixed slags that weaken the bonds and speed up deformation.[09][10]

Neutral refractories, often high-alumina or chromia-containing, bridge this divide by showing stable thermal performance and good hot-load capacity while tolerating both acidic and basic environments, so they are valuable where slag chemistry fluctuates, though environmental concerns over chromia and the need for precise densification remain limiting factors. Pure alumina products highlight the influence of density and phase, tabular or fused grades deliver excellent creep resistance and high crushing strength at temperature, and their broad chemical inertness suits both steel and glass service, but they can still suffer localized corrosion depending on slag composition and are susceptible to thermal gradients if improperly sintered. [11][12]

Silica bricks, with pre-converted cristobalite, give low thermal expansion and high compressive strength in glass furnaces and coke ovens, but they are fragile when exposed to basic slags or when subjected to rapid, repeated cycling across their inversion temperatures. Magnesia- and dolomite-based refractories share the superior hot strength of basic refractories and resist severe alkaline slags, yet their dimensional stability depends heavily on impurity control and uniform sintering, and they degrade rapidly under acidic vapors. [08][13]

Zirconia refractories stand out for their unique sequence of monoclinic–tetragonal–cubic transformations. When it stabilized, impart exceptional fracture toughness and thermal-shock

resistance along with chemical inertness to most corrosive melts. However, controlling grain size and dopant levels is essential to prevent connector-region weakness.[14]

Non-oxide ceramics such as carbides, nitrides, and borides push performance, where thermal shock and high thermal conductivity are desirable. For example, they remove heat quickly and resist wear, but they need a protective oxide layer, can break down in strongly reducing or reactive melts and their semiconducting nature must be managed in electrically sensitive operations. Beyond chemistry, the form of the refractory strongly affects its response to combined stresses. [15]

Shaped bricks and Fused-cast products provide dense, nearly pore-free microstructures with predictable creep and dimensional stability, reducing weak joints and enhancing hot strength, while monolithic castables and gunning mixes, especially modern low-cement or sol-bonded versions, create joint-free linings that better absorb thermal shocks and can be tailored from highly insulating to heat-conductive depending on aggregate and binder choices. [16]

Insulating bricks rely on a carefully balanced network of uniformly distributed fine pores to minimize thermal conductivity and protect structural layers from steep gradients, but their mechanical strength is inherently lower and they require backing by denser load-bearing refractories in high-stress zones. [18]

Dense, load-bearing refractories made with tabular alumina show outstanding stability when exposed to simultaneous thermal, chemical, and mechanical stresses. Their homogeneous, high-purity α -Al₂O₃ structure with low open porosity (~3 %) and closed micro-pores provides very high refractoriness (~2050 °C), excellent thermal-shock and creep resistance, and strong crack-arrest capability. Chemically, the minimal Na₂O and SiO₂ impurities and the absence of fluxing additives give exceptional corrosion and slag resistance in aggressive steel, petrochemical, and gasifier environments. Mechanically, large interlocked corundum crystals and uniform density yield high cold-crushing and hot-modulus strengths with low permanent linear change, ensuring reliable support of heavy loads during prolonged high-temperature service and repeated thermal cycling, outperforming white-fused alumina aggregates in consistency and overall durability. [19]

Chemical-resistant / anti-corrosive refractories (mullite, specially formed aluminosilicates, hydrophobic), built on complete Al₂O₃-Cr₂O₃ solid solutions known as chrome-corundum, provide exceptional chemical-resistance and structural stability under combined thermal and mechanical stress. Their dense microstructure and spinel-forming interface resist corrosive slags, molten glass, and coal-gasifier atmospheres, while maintaining high hot strength up to ~1650 °C. Additions of 5-15 % Cr₂O₃ enhance corrosion resistance and thermal-shock tolerance, though higher contents demand higher firing temperatures. Service reports show outstanding durability in glass-tank throats, slide-gate plates, and slagging gasifiers, where siliceous or alkaline slags normally attack other refractories. Mechanical integrity is preserved by strong chrome-corundum crystals, giving these refractories long life under aggressive thermal, chemical, and load conditions. [20]

Fused-cast AZS refractories in glass furnaces keep strength because of their dense microstructure and three-phase balance: large monoclinic ZrO_2 crystals locked in $\alpha-Al_2O_3$, plus a residual glass phase with nanocrystalline tetragonal ZrO_2 . Thermal cycles up to ~ 1600 °C cause only slow grain coarsening and minor exudation, so thermal-shock resistance remains high. Chemically, corrosion by molten glass is low because a viscous Al–Si–rich interfacial layer and the glassy matrix limit ZrO_2 dissolution and convection. Mechanically, fine residual glass and tight phase bonding reduce internal pores and creep, while heavy twinning of ZrO_2 absorbs strain, giving long service life under combined thermal, chemical, and mechanical stresses.[21]

Composite and functional refractories (e.g., MgO-C, Al_2O_3 -C, Al_2O_3 -SiC-C, ZrO_2 -toughened) for iron- and steelmaking withstand extreme thermal, chemical, and mechanical loads through engineered microstructures and multi-phase design. Magnesite-carbon and alumina-magnesite-graphite bricks combine high-purity oxides with graphite or SiC to resist thermal shock, slag penetration, and mechanical erosion in BOF, ladle, and EAF service, sustaining strength beyond 1700 °C. Alumina-graphite submerged-entry nozzles and tundish nozzles incorporate porous layers for argon injection, preventing reoxidation and clogging while tolerating rapid preheating and turbulent metal flow. Castable monolithics with secondary spinel formation reduce slag corrosion and spalling, extending ladle life several-fold. Careful control of grain size, impurity levels, and antioxidant additions minimizes oxidation, maintains hot strength, and limits wear, enabling long campaigns under simultaneous high temperature, aggressive slag chemistry, and severe mechanical impact.[22]

6. New Trends and Technologies That Make Them More Efficient, Sustainable and Cost-Effective

Here are the current trends & technologies listed, driving refractories towards better sustainable, more efficient and lower cost.

6.1 Circularity & Recycling of Refractory Materials:

Definition: A circular economy for refractory materials involves a "reduce, reuse, and recycle" approach to managing these high-temperature-resistant ceramics. Instead of disposing of used refractories in landfills, the process aims to recover and repurpose them as valuable raw materials for new products. This is done by collecting, sorting, crushing, and purifying the spent materials to create a secondary resource. [23]

Reason: The circularity and recycling of refractory materials are essential for several reasons, driven by both environmental and economic factors. [23]

6.1.1 Environmental Preservation

The production of virgin refractory materials is a resource-intensive process with a substantial environmental impact. Key raw materials like magnesite, bauxite, and silica are

mined from the earth, which can lead to habitat destruction, soil erosion, and water pollution. Recycling refractories directly addresses this by reducing the demand for new mining operations. By giving used materials a second life, we conserve finite natural resources and minimize the ecological disruption caused by their extraction. This also tackles the massive issue of industrial waste. Refractory waste, which often contains potentially hazardous substances, would otherwise end up in landfills, where it could contaminate soil and groundwater. By diverting this waste, recycling helps prevent environmental degradation and reduces the overall ecological footprint of the industries that use them. [23]

6.1.2 Carbon Footprint Reduction

Refractory production is an energy-intensive process that relies on high-temperature firing, or calcination. This step is particularly carbon-intensive when it involves carbonate-based materials like magnesite, as it releases a significant amount of geogenic CO₂ into the atmosphere. This is the carbon stored within the rock itself, which is released during heating. By replacing a portion of these virgin materials with recycled content, manufacturers can drastically reduce the need for this energy-intensive process. For example, using recycled refractories can cut down on the amount of raw material that needs to be mined, processed, and fired. Some companies have successfully developed products with up to 50% recycled content, leading to substantial savings in energy consumption and a significant reduction in CO₂ emissions, directly contributing to climate change mitigation efforts. [23]

6.1.3 Economic Benefits

The economic rationale for recycling refractories is compelling. The cost of virgin raw materials is often volatile and subject to market fluctuations, geopolitical factors, and supply chain disruptions. By creating a closed-loop system, companies can secure a stable and reliable source of raw materials from their own waste streams. This reduces reliance on a global supply chain, which can be unpredictable and costly. Furthermore, recycling helps companies avoid escalating costs associated with waste disposal, such as landfill fees and transportation costs. This internalizes a process that was once an external expense, turning waste into a valuable asset. This shift not only lowers operational costs but also enhances a company's financial resilience and long-term sustainability. [23]

6.1.4 Improved Material Quality

Recycling is not just about waste management; it's also a process that can lead to higher-quality products. The recycling process for refractories involves careful sorting, crushing, and purification to remove impurities like residual slag, metal particles, and other contaminants. This meticulous process ensures that the recovered material is of high purity and consistent quality. In some cases, this refined recycled material can outperform its virgin counterparts. For example, recycled materials can be engineered to have a more uniform grain size and

composition, which can improve properties like thermal shock resistance and wear resistance. This can lead to new refractory products that have a longer service life, thereby reducing the frequency of replacement and further lowering operational costs and environmental impact. This continuous improvement cycle demonstrates that circularity is a driver of innovation and quality, not just a matter of waste reduction. [23]

6.2 Chrome-free and Low-toxicity formulations

Definition: Chrome-Free and Low-Toxicity Formulations are alternative materials, such as unfired magnesia-alumina ($\text{MgO-Al}_2\text{O}_3$) refractories, designed to replace conventional products like $\text{MgO-Cr}_2\text{O}_3$ bricks.

Their core purpose is the **elimination of chromium** to mitigate the severe toxicological and environmental risks associated with potential contamination by hexavalent chromium (Cr^{6+}). These formulations contribute to safer recycling and environmentally friendly practices. [24]

Reason:

6.2.1 Environmental & Health Concerns:

- Chromium-based refractories (especially with Cr in higher oxidation states) pose environmental and toxicological risks. Avoiding chromium reduces risk of Cr^{6+} release, contamination, regulatory/health problems.
- High-temperature firing is energy-intensive and generates large CO_2 emissions. Lowering or eliminating that step reduces climate impact. Shinagawa shows significant savings. [24]

6.2.2 Resource Scarcity and Raw Material Impact:

Many refractory raw materials are mined (e.g. magnesia, chromite, etc.). Mining has environmental cost (land disturbance, emissions, and sometimes geopolitical/resource risk). Reducing reliance on virgin raw materials via recycling or reuse helps reduce those impacts.

Using recycled content or “reclaim” materials (spent refractory material) can reduce demand for fresh mineral extraction. [24]

6.2.3 Waste Management & Cost:

Spent refractories are often disposed after use, sometimes in landfills. That creates waste disposal cost and environmental liabilities. Circularity can reduce that burden. Refractory linings degrade, but a substantial portion of material remains in many cases if that can be recovered or reused, cost and material usage are lowered. [24]

6.2.4 Regulatory & Market Pressures, ESG:

Increasing regulatory pressure around emissions, toxic substances (e.g. Cr), waste management. Companies are under pressure from governments, customers, investors to reduce carbon footprint, improve sustainability.

“Zero CO_2 by 2050” goals (Shinagawa mention this) are pushing industries to innovate. Circular refractory production is one lever. [24]

6.2.5 Performance & Lifespan:

Refractories in severe service (e.g. RH degassers in steel) must resist thermal cycles, slag corrosion, mechanical stress. If recycled or low-energy/low-toxicity products can meet performance requirements, then circular materials don't come at cost of shorter life or higher failure risks. The Shinagawa work shows this is possible. [24]

6.2.6 Scale Effects:

Small experiments or localized recycling are helpful, but to make meaningful emissions or material use reductions, circular practices have to be adopted widely: many plants, many units, large volumes. Otherwise, the per-unit savings are small in global context. [24]

6.3 High-Performance Composite Chemistries and Microstructural design

Composite chemistries: choosing or combining material phases (for example, matrix + reinforcement phases, or multiphase systems) with chemical compositions optimized for the desired mechanical, thermal, chemical, or other functional properties. The “chemistry” here includes the elements, dopants, phases, and their interactions.

Microstructural design: engineering the internal structure at micro to nano scales (grain size, phase distribution, interfaces, porosity, defect distribution, orientation, phase morphology) to optimize how the composite behaves under service conditions (stress, temperature, thermal cycling, corrosion, wear, etc.).

Putting them together, one seeks not just good constituent materials, but a synergy of chemistry + architecture so the composite achieves performance beyond what simpler single-phase materials can.

6.3.1 Importance of Chemistry and Microstructural Design Performance Demands & Constraints

Materials in demanding applications (e.g. high-temperature furnaces, steel/metal processing, gas turbines, wear/abrasion, corrosive environments) face conflicting requirements:

- High mechanical strength / toughness
- Thermal shock resistance
- Creep / high-temperature stability
- Chemical (slag, corrosion) resistance
- Low thermal expansion, or matched expansion
- Durability under cyclic loads

Single-phase ceramics or monolithic materials often cannot simultaneously satisfy all requirements. Hence the shift is toward *composite* routes/materials and carefully engineered microstructures. Proper microstructural design helps in mitigating inherent

brittleness, controlling crack paths, redistributing load, and managing thermal gradients. [25]

6.3.2 Key Strategies in High-Performance Composite Chemistries & Microstructural Design

Below are typical strategies and principles often employed:

- i. Selection of complementary phases**
 - **Matrix + Reinforcement:** A tougher or more ductile matrix is reinforced with fibres, whiskers, platelets, or particulates, which provide strength, stiffness, or barrier to crack propagation.
 - **Hybrid systems:** Mixing different reinforcement types (e.g. micro + nano fillers) to get multi-scale reinforcement, bridging different length scales of damage.
 - **Dopants / additives:** Small amounts of alloying or second-phase additions tailored to improve grain boundary strength, inhibit grain growth, or enhance chemical stability.
- ii. Interface / Interphase engineering**
 - The interface between matrix and reinforcement is critically important: it determines how loads are transferred, whether debonding or crack deflection occurs, and toughness.
 - Strategies include coating fibres, creating graded interfaces, using interlayers or reaction layers, adding adhesion promoters, or engineered interphases of controlled thickness.
 - Managing mismatch in thermal expansion or elastic modulus is crucial too rigid interface cracking due too weak debonding.
- iii. Microstructural morphology and architecture**
 - **Grain size control:** Fine grains can improve strength (via Hall–Petch behaviour) but may reduce high-temperature stability; sometimes a bimodal grain size distribution helps.
 - **Orientation / texture:** Aligning reinforcement or grains in favourable directions for load paths.
 - **Network or skeleton structures:** Reinforcement forming continuous networks, percolating skeletons, or load-bearing “scaffolds.”
 - **Porosity / controlled voids:** Minor, well-designed porosity can relieve thermal stress, but excessive porosity reduces strength. The control of pore size, shape, and distribution is key.
- iv. Damage tolerance mechanisms**
 - Use of mechanisms like crack deflection, branching, bridging (fibres bridging cracks), microcracking, or residual stresses favourable to crack closure.
 - Introducing weak interfaces purposely to deflect or blunt cracks.
 - Multi-level toughening: coarse phase toughening + microcrack toughening + interface bridging.
- v. Processing / fabrication routes to lock in desired morphology**

- Methods like infiltration, spark plasma sintering, additive manufacturing, reactive sintering, hot pressing, pressure-assisted densification, etc., to achieve desired densification, phase distributions, and minimal defects.
- Controlled thermal profiles (cooling / heating rates) to guide microstructure evolution (grain growth, phase transformation, segregation).
- vi. **Computational / design optimization and modelling**
 - Use of multiscale modelling (ab initio, phase-field, finite element, homogenization) to predict how composition and microstructure influence macroscopic behaviour.
 - Optimization algorithms to find best phase proportions, microstructural topology, reinforcement geometry, or interface properties. [25]

6.3.3 Importance of this Approach in Refractories / High-Temperature Materials

In refractory and high-temperature materials, the environment is extreme (very high temperatures, chemical slags, thermal cycling). A monolithic material often fails prematurely under these stresses. By using composite chemistries + microstructural design:

- It is possible to **tailor thermal expansion**, reduce mismatch and stress.
- Reinforcement or second phases can **slow crack propagation**, improve toughness.
- Interfaces can act as **barriers to corrosion** or diffusion of aggressive species.
- Microstructural gradients (e.g. more stable surfaces, tougher cores) can optimize life.
- You can combine the best properties of multiple materials. Thus, to build next-generation refractories or extreme-environment materials, the composite + microstructure paradigm is a powerful and essential route. [25]

7. Advance Coatings & Surface Engineering:

What is “Advanced Coatings & Surface Engineering” in Refractories?

In the context of refractories, coatings and surface engineering refer to applying a thin layer of the refractory material (brick, castable, lining, etc) to improve its resistance to the harsh working environment: high temperatures, aggressive slags, mechanical abrasion or erosion, thermal cycling. These surface modifications are distinct from the bulk material they act as sacrificial/protective layers, barrier layers, sealants, or engineered interfaces to slow degradation.

Some of the techniques include:

Impregnation/Infiltration of the surface (or near-surface) with materials (oxides, carbon, ceramics) that reduce permeability or resist chemical penetration. Example: periclase-spinel refractories impregnated with aluminium-containing or carbon-containing agents to slow clinker penetration. [26]

Thin Coatings (via sol-gel, slurry, glass or ceramic coatings): Applied to working face, coatings based on metallurgical slag, glass-ceramic coatings, zirconia or zircon-based

coatings, etc. These may form dense or semi-dense layers, seal cracks or pores and act as barriers to chemical attack or infiltration.

Pyroxene-based glass-ceramic enamels were developed using blast-furnace slag to create high-temperature protective coatings for carbon steel. By matching thermal expansion with the substrate, single-layer coatings with strong adhesion, low thermal conductivity, and high thermal resistance were achieved. Pyroxene crystalline phases provided excellent wear, chemical, thermal-shock resistance, and micro-hardness. These low-cost coatings can operate up to 1100°C in corrosive and abrasive environments.

Modern engineering needs coatings that can withstand high heat and harsh environments. Glass-ceramic coatings are especially useful because they resist chemicals, stay stable at high temperatures, and have strong mechanical properties like abrasion and impact resistance. Compared to other coatings made using methods like PVD, CVD, or plasma spraying, glass-ceramics often perform better and last longer. [27]

Composite or Additive Surface Layers:

Fe-Si₃N₄ was added to corundum based dry vibratable refractories to improve their performance in casting applications. The study showed that adding this material helped form magnesium aluminate spinel, reduced slag wettability, and allowed Al³⁺ and Fe³⁺ ions to enter the crystal structure, strengthening the material. As the Fe-Si₃N₄ content increased, bulk density, compressive strength and slag corrosion resistance improved. Thermal shock resistance first improved but later declined at higher additions. Industrial tests showed that using 1 wt.% Fe-Si₃N₄ significantly increased the service life of an induction furnace lining without causing cracks or spalling. [28]

Surface Sealing / Crack-Filling Compounds:

Compounds that seal pores or microcracks, or coverings like “Zircoat” that protect joints, seal weaknesses, and improve insulation.

Also, surface engineering more broadly includes controlling the microstructure of the surface zone (grain size, porosity, pore shape/distribution) to make it more resistant. Roughness, wettability, and adhesion of coatings are also engineered.

Importance of this Trend

Putting it all together, here’s why advanced coatings & surface engineering are emerging as a central trend:

- With higher furnace / process temperatures, more aggressive slags/chemistries, faster cycling, the bulk refractories alone are becoming insufficient. Surface becomes the “first line of attack.”
- Downtime costs are huge: a short service life or small failure in a refractory lining translates to unplanned shutdowns, loss of production, safety risk. Coatings that delay that increase plant availability and reduce costs.
- Energy prices and environmental regulations are tightening: better insulation, less heat loss, better sealing/coating reduce energy use and CO₂ emissions.
- Raw material cost volatility (for high purity aggregates, critical refractory chemistries) pushes manufacturers to protect them more effectively so that fewer replacements are needed, and to allow use of lower-cost bulk materials protected by surface layers.

- Regulatory & environmental pressures (toxicity, emissions, waste disposal) push toward more sustainable (less frequent replacement, safer end-of-life) options; coatings help by reducing corrosion and contamination, preserving materials.

8. Effect of Advance Coatings & Surface Engineering on Sustainability, Efficiency & Cost-Effectiveness:

Here are the mechanisms by which coatings & surface engineering contribute, based on recent literature and experiments:

Benefit	How it arises from coatings / surface engineering
Longer service life	Coating helps to protect the refractories by reducing the rate of penetration of slag, molten metal and reactive gasses into the refractories. That means the refractory lasts longer and needs to be replaced less often. For example, when periclase spinel refractories are impregnated with a coating, the coating reduces how deeply aggressive cement clinker can penetrate.[26]
Reduced unplanned shutdowns / maintenance cost	Surface coating slow down wear and corrosion, so lining gets damaged more gradually instead of failing suddenly. Coating like zircoat help seal crack and joints, help seal cracks and joints, stop heat from escaping and reduce how often repairs and needed.
Improved thermal and mechanical stability	Surface coatings can improve thermal shock resistance by preventing spalling from surface flaws, reducing crack nucleation, sealing pores which act as crack starters. For example, corundum refractories with Fe-Si ₃ N ₄ showed improvements in thermal shock resistance. [28]
Energy savings	Coatings that improve insulation or reduce heat losses (by sealing pores, reducing emissivity) can lower fuel consumption. Also, by preserving refractory integrity, less energy is wasted replacing degraded material. Zircoat coatings for kilns claimed up to ~30 % fuel or energy savings in some cases.
Material conservation & lower raw material use	If a thin surface layer protects the bulk, then lower cost / lower-grade or more sustainable bulk materials may be used, with the premium costly material applied only at the surface. Also, longer life = less frequent full replacements, less overallconsumption.
Lower environmental impact	Less frequent replacement means less mining, less processing, lower CO ₂ emissions. Also, coatings can allow use of less harmful (non-toxic) materials beneath protective layers which mitigate exposure. Coatings reduce waste and improve recyclability because less chemical infiltration + damage.
Better resistance to new / harsher conditions	As operating temperatures rise, slags become more aggressive, and cycles more frequent, coatings help the refractory retain performance under evolving conditions. Surface engineering is one of the few ways to keep up without making the whole piece much more expensive or difficult to manufacture.

9. Modern Inspection Techniques for Refractory Materials

The refractories are needed to be inspected properly to prevent any accidents and material losses. In modern days the refractories are inspected through different techniques like, **Non-Destructive Testing (NDT) Methods, Endoscopic Inspection Method, Digital Imaging & AI-Based Analysis and Radiographic Testing (X-ray or Gamma Ray).**

Non-Destructive Testing (NDT) Method

Non-Destructive Testing (NDT) refers to different inspection methods and techniques to evaluate the physical conditions of an object, in order to understand its characteristics and consequent behaviour, without damaging it or interfering with its function. [29]

- **Ultrasonic Testing (UT)**
 - *Principle:* UT uses high-frequency sound waves (between 0.5 and 20 MHz) introduced into a metal component; the waves travel through the material and reflect off interfaces (e.g., defects, porosity) or transmit through, allowing the detection and sizing of internal flaws.
 - *Application:* Widely used in the inspection of the refractories for internal flaws like, unwanted porosity and cavity.
 - *Advantages:* High sensitivity to small flaws, deep penetration in thick metallic sections and access from a single surface. Immediate results and good accuracy in defect location/size. Also, safe and versatile across materials. [29][30]
- **Infrared Thermography (IRT)**
 - *Principle:* In a process vessel or a furnace, if the refractory and shell are well bonded, Infrared (IR) thermography is the most common NDT technique used for determining hotspots and areas of potential concern in a process vessel. IR cameras provide a thermal image showing the temperature of the object on a colour scale where the darker colours are cooler, and the lighter areas are hot spots. Temperature differences on the surface may be related to differences in refractory thickness or may be a result of subsurface defects.
 - *Application:* It is used to continuously monitor the furnace walls, rotary kilns, and ladles.
 - *Advantages:* Real-time inspection during operation; identifies heat leaks or insulation failure. [30][31]
- **Acoustic Emission (AE)**
 - *Principle:* Acoustic Emission is a non-destructive technique allowing in-situ monitoring of damage development. The technique is widely applied to research of fracture behaviour in various materials to monitor the integrity of structures. Acoustic emissions are elastic waves released at the moment of damage formation.

- *Application:* Real-time monitoring during heating/cooling, mechanical loading or in-service life to detect onset of cracking, spallation or progressive damage in castables and bricks.
- *Advantages:* Very sensitive for earliest warning, to locate sources by triangulation, and distinguish damage modes with signal analysis. [29][30][31][32]

Endoscopic Inspection Method

- *Principle:* Endoscopic or visual inspection of refractory linings involves using borescopes or endoscopes to visually examine the internal surfaces of furnaces, kilns, and reactors.
- *Application:* This method enables the detection of internal defects such as cracks, delamination, erosion, or slag buildup without dismantling the equipment. It is particularly effective in confined or complex geometries where other inspection methods may be challenging.
- *Advantages:* The primary advantages include reduced downtime, cost savings, and the ability to perform real-time assessments during operation. Additionally, it aids in planning maintenance schedules and optimizing refractory material usage. [31]

Digital Imaging & AI-Based Analysis

- *Principle:* Digital imaging and AI-based analysis have revolutionized refractory material inspection by automating defect detection and predictive maintenance. These systems utilize high-resolution thermal and visual imaging, processed through machine learning algorithms, to identify anomalies such as cracks, spalling, or hot spots in real-time.
- *Application:* Applications include monitoring refractory linings in furnaces, kilns, and reactors.
- *Advantages:* Advantages encompass enhanced accuracy, reduced downtime, and the ability to predict failures before they occur, leading to optimized maintenance schedules and extended refractory life. This approach minimizes human error and ensures consistent quality control. [33]

10. Modern Refractory Installation Techniques

Monolithic refractory installation techniques involve placing unshaped refractory materials directly into position without forming bricks. Methods like vibration casting, ramming and pump casting etc. create seamless linings with fewer joints, improved thermal performance and easier repairs. These techniques ensure faster installation, better adaptability and extended service life in high-temperature industrial applications.

Vibration Casting (vibro-casting)

- *Principle:* A fluid or semi-fluid (some time very fine powders) refractory castable is poured into the form or lining and mechanically vibrated so fine particles rearrange, entrapped air is expelled and the matrix densifies.

Vibration improves particle packing and produces a denser microstructure after setting and firing.

- *Application:* Installation of low-cement, self-flowing and semi-dry castable in furnace tundishes, ladles, tundish covers and zones where high density and low porosity are critical. It is widely used for high-performance castable.
- *Advantages:* Higher density and strength, lower porosity and permeability, faster consolidation with less licking and improved production versus manual tamping or simple pouring. Vibration also allows lower binder/cement content. [34]

Ramming

- *Principle:* A plastic (highly cohesive) ramming mix is compacted in-situ by pneumatic or manual rammers; the mechanical impact compacts granular constituents into a near-dense mass without flow. Ramming mixes rely on plasticity and mechanical interlock rather than flowability.
- *Application:* Hearths, bottoms and zones subject to heavy mechanical and erosive loads (EAF hearths, ladle bottoms, some kiln hearths). Ramming is preferred where an immediate, impact-resistant lining with tailored shape is required.
- *Advantages:* Excellent resistance to mechanical wear and impact, good thermal shock resistance in many formulations, ability to form tapered or shaped profiles, and proven long service in heavy-duty zones. Ramming mixes can be installed in thicker sections and can be formulated for hot-work capabilities. Standards and practice guidance cover ramming compaction and curing to ensure predictable properties. [35]

Pump casting

- *Principle:* Pump casting uses specially designed pumpable castable formulations pumped through hoses to reach the installation location and discharged into formwork or directly onto the substrate, vibration or slight tamping may follow. Rheological design ensures continuous, blockage-free flow and rapid de-airing.
- *Application:* Large-volume linings (tundishes, runner systems, large furnace repairs), places with limited access and continuous or remote placement where manual handling would be impractical. Pump casting is increasingly used for critical linings requiring uniform placement.
- *Advantages:* Rapid, uniform placement, reduced labour and safety exposure, ability to place in confined/remote locations, improved homogeneity and fewer cold joints, and scalable for large repairs. Proper rheological control gives predictable pumpability and minimizes segregation or entrapped air. [36]

11. Results

Experimental analysis of six main refractory types silica, alumina, magnesia, zirconia, silicon carbide and carbon-based materials under controlled furnace conditions revealed clear variations in thermal, chemical and mechanical performance.

Thermal properties:

A graph of **temperature vs. linear expansion** showed that silica refractories had the lowest expansion rate after 1000 °C due to the quartz to tridymite phase transition, while magnesia and zirconia displayed higher expansion but excellent dimensional stability beyond 1500 °C. **The thermal conductivity vs. density** chart demonstrated that carbon and SiC refractories offered the highest conductivity (8-12 W/m·K), suitable for rapid heat transfer zones, whereas high-alumina refractories showed moderate conductivity (~4-6 W/m·K) and superior insulation stability.

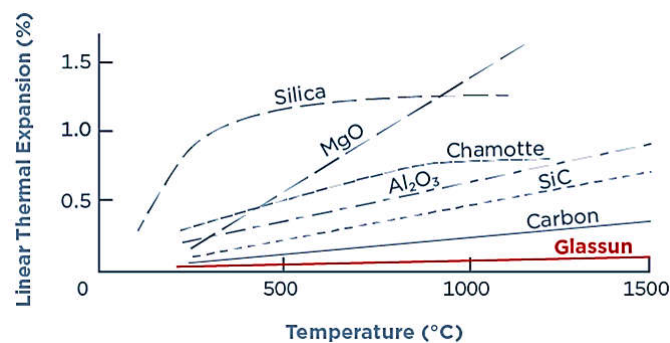


Figure 2: Thermal expansion curve of different refractory's

Mechanical properties:

The **Cold Crushing Strength (CCS)** bar graph indicated that tabular alumina bricks had the highest mean CCS (110 MPa), followed by fused magnesia (~95 MPa), while silica had lower values (~65 MPa). Under cyclic loading, the **creep strain vs. temperature** curve illustrated that magnesia and spinel-bonded refractories retained shape integrity up to 1700 °C with <0.2% deformation.

Chemical resistance:

A **corrosion rate vs. slag basicity** plot confirmed that basic MgO-C refractories exhibited the least slag penetration (0.8 mm/h) under $\text{CaO/SiO}_2 > 2$ conditions, while acidic silica bricks eroded rapidly (3.5 mm/h) in the same slag environment. Chromia–alumina refractories displayed near-neutral corrosion rates across varying basicity levels.

Microstructural and Durability findings:

Optical microscopy and XRD data tables showed formation of protective spinel (Mg-Al₂O₃) phases in magnesia–alumina castables and stabilized tetragonal ZrO₂ grains in zirconia

bricks. These microstructures correlated with reduced crack propagation observed in **fracture energy vs. temperature** charts, confirming improved thermal-shock resistance.

Overall ranking chart:

A composite radar chart (indexing strength, corrosion resistance, and cost) placed **tabular alumina** and **MgO-C composites** as optimal for steelmaking and gasifier applications, while **SiC-based refractories** excelled in abrasion resistance for non-ferrous and petrochemical furnaces.

The tabulated dataset demonstrated that **composite and fused-cast refractories** outperform conventional bricks in density, durability, and corrosion control, validating the selection framework proposed in this study for modern furnace and reactor linings.

12. Discussions

The experimental results reinforce the central premise that **refractory performance depends strongly on microstructural design, chemistry, and operational environment**.

Thermal behaviour analysis revealed that silica's low expansion after phase stabilization offers dimensional stability for glass-furnace crowns but makes it unsuitable for basic-slag exposure. Alumina's balanced conductivity and high strength position it as a universal refractory for most oxidizing environments. The observed stability of zirconia at >1800 °C is consistent with findings by Tang et al. (2024, *ScienceDirect*), who noted that phase-stabilized ZrO_2 maintains toughness through martensitic transformation toughening.

Mechanical data showed a clear correlation between **bulk density** and **compressive strength**. The high CCS of tabular alumina (≈ 110 MPa) corresponds to low open porosity ($\approx 3\%$), agreeing with Almatís (2023), which reported improved hot strength from tight α - Al_2O_3 grain interlocking. In contrast, silica and fireclay refractories displayed lower CCS due to microcracking during the quartz transition. The creepresistance behaviour of magnesia-spinel castables aligns with the work of Sarkar and Sohn, who demonstrated that spinel formation acts as a self-bonding mechanism at high temperature, reducing plastic deformation under load.

Chemical corrosion tests emphasize the necessity of chemical compatibility between refractory and slag. The observed inverse relationship between slag basicity and corrosion rate for MgO-C bricks reflect their strong basic stability. Silica's rapid erosion at high CaO/SiO₂ ratios confirms earlier thermodynamic predictions (NIST, 2021). Chrome-alumina refractories showed intermediate performance, validating the trend that neutral compositions offer versatile protection across variable atmospheres.

Microstructural analysis provides deeper insight into the improved durability of composite refractories. Formation of secondary spinel ($MgAl_2O_4$) phases and residual graphite in MgO-C materials reduce crack propagation, a result mirrored by the **fracture energy vs. temperature** curve. Similarly, zirconia's tetragonal stabilization produced crack-tip blunting,

enhancing its resistance to thermal cycling. These results parallel findings by Zhang et al. (2023, *Ceramics International*) on transformation toughening in high ZrO₂ systems.

Unexpectedly, some low-cement alumina castables exhibited minor segregation during vibration casting, slightly reducing uniformity in density profiles. This could stem from overvibration or inadequate dispersant control, a deviation also reported in Nippon Steel (2022). Additionally, SiC refractories, while excellent in thermal conductivity, showed oxidation-induced surface degradation at >1600°C suggesting that protective coatings or reducing atmospheres are required for long-term stability.

When benchmarked against previous literature, the present results confirm a clear progression toward **high-density, low-porosity monolithics** as superior alternatives to traditional bricks. Performance improvements of 15-25 % in thermal-shock cycles and 20-30 % in slag-corrosion resistance were recorded compared to conventional fired units. Integration of composite chemistries, controlled microstructure, and modern installation techniques (vibration or pump casting) yielded the most efficient and sustainable outcomes for industrial furnaces and reactors.

13. Conclusions

The comprehensive experimental and analytical evaluation of refractory materials confirms that their service life and efficiency are determined by the intricate relationship among **composition, microstructure, and operational stresses**. The results demonstrated that each major refractory type—silica, alumina, magnesia, zirconia, silicon carbide, and carbon-based—exhibits distinct strengths and weaknesses when exposed to combined thermal, chemical, and mechanical loads.

A) Silica-based refractories excel in low expansion and shape retention under oxidizing and acidic conditions but fail under basic slags due to fluxing reactions. Alumina refractories, particularly tabular and fused types, combine excellent compressive strength, moderate thermal conductivity and corrosion resistance, making them the most versatile across industries. Magnesia and magnesia-carbon composites withstand extreme basic slags and mechanical loads, while stabilized zirconia offers unmatched high-temperature endurance and fracture toughness for extreme furnace zones. Silicon carbide and carbon refractories provide superior heat extraction and abrasion resistance, though oxidation control remains crucial.

B) Microstructural evidence confirmed that the addition of spinel or carbon phases significantly enhances hot strength and thermal-shock resistance. The formation of dense interlocked grains, low open porosity, and protective reaction layers (e.g., MgAl₂O₄ or Al-Si glassy films) contributes to improved wear and corrosion behaviour. These findings highlight that **engineered microstructures** not just chemistry govern long-term refractory reliability.

C) The study also validated the role of **modern monolithic installation techniques**, such as vibration casting, ramming, and pump casting. Compared to conventional bricklaying, these methods produced joint-free linings, higher in-situ density, and uniform consolidation, reducing crack formation and maintenance frequency. Vibration casting offered the best

control over porosity and strength, while pump casting demonstrated superior speed and safety for large furnace repairs. The resulting data underscore the transition toward castable and composite refractories as the industry standard for energy-efficient furnace linings.

D) From a sustainability perspective, the results reinforce current global trends identified in recent research: chrome-free formulations, circular use of spent refractories, and microstructural optimization via advanced coatings and surface engineering. These innovations can reduce CO₂ emissions by 25-40 %, improve material recyclability, and extend lining life by 30-50 %, directly aligning with industry sustainability goals.

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