www.ijarp.com ISSN 2456-9992 Page: 01-43

International Journal Advanced Research Publications

Research Article

Volume: 02
Issue: 07

REFRACTORY MATERIALS IN CEMENT AND CERAMIC INDUSTRIES: CLASSIFICATIONS, PROPERTIES, TESTING METHODS, AND INDUSTRIAL APPLICATIONS

***Shiva Kant Jha, Aum Garg, Amit Kumar Meena, Bhupendra Singh Ken, Mukul Vijay, Kapil Nahar, Neetesh Kumar Dehariya**

Department of Ceramic Engineering, Mewari University, Chittorgarh, Rajasthan, India.

Article Received: 07 June 2026, Article Revised: 27 June 2026, Published on: 17 July 2026

***Corresponding Author: Shiva Kant Jha**

Department of Ceramic Engineering, Mewari University, Chittorgarh, Rajasthan, India.

Doi: https://doi-doi.org/101555/ijrpa.3756

ABSTRACT

Refractory materials are indispensable components of high-temperature industrial systems, serving a critical role in sectors such as cement manufacturing, glass production, and advanced ceramics processing. These specially engineered materials are designed to endure extreme thermal loads, aggressive chemical attack, mechanical stresses, and prolonged operational conditions while preserving their structural stability and functional performance. This review presents a comprehensive evaluation of refractories through seven key perspectives: classification approaches based on chemical composition, manufacturing processes, physical form, porosity, service temperature, purity level, and specialized applications; physicochemical and thermo-mechanical properties; degradation and corrosion mechanisms; testing and characterization techniques; industry-specific application zones; quality-control challenges; and emerging developments focused on sustainability.

Particular attention is devoted to the performance assessment of major refractory systems, including alumina, magnesia-spinel, alumina-zirconia-silica (AZS), silicon carbide, and fused-cast refractories employed in cement rotary kilns, preheaters, calciners, coolers, and glass-melting furnaces. The review integrates quantitative property data, manufacturing methodologies, microstructural characteristics, and prevalent failure mechanisms within the framework of internationally accepted standards such as ISO, ASTM, and EN. Furthermore, critical research gaps are identified, including the need for advanced predictive models of thermochemical degradation, environmentally benign chromium-free alternatives for basic

refractory applications, and the development of low-carbon refractory technologies based on low-cement castables and geopolymer systems.

Looking ahead, the future of refractory technology is expected to be shaped by the convergence of computational materials engineering, additive manufacturing, real-time digital monitoring, and circular-economy strategies. These innovations have the potential to enable the development of sustainable, high-performance refractory solutions capable of supporting energy-efficient and carbon-neutral industrial operations.

KEYWORDS: Refractories; Cement Industry; Glass Furnaces; Alumina Refractories; Magnesia-Spinel Refractories; AZS Refractories; Corrosion Resistance; Thermal Shock Resistance; Monolithic Refractories; Sustainable Materials.

1. INTRODUCTION TO REFRACTORIES

1.1 Definition, Importance, and Historical Context

Refractory materials are broadly defined as non-metallic substances capable of withstanding temperatures exceeding 1,500 °C (2,732 °F) without significant deformation, melting, or deterioration of their structural and functional properties.[1][2][3] The International Organisation for Standardisation (ISO 836:2015) characterises refractories as materials whose pyrometric cone equivalent (PCE) is not less than 1,500 °C.[18] Beyond this temperature threshold, refractories must also resist chemical attack from slags, molten metals, alkaline vapours, and corrosive gases that inevitably accompany high-temperature manufacturing operations.

The global refractory market was valued at approximately USD 30.2 billion in 2023 and is projected to reach USD 42.8 billion by 2032, driven predominantly by growth in the steel, cement, glass, non-ferrous metals, and petrochemical sectors.[27] Cement production alone accounts for approximately 4–5 billion metric tonnes annually, requiring substantial refractory lining investments for rotary kilns, preheaters, calciners, and clinker coolers.[33] A single large cement rotary kiln of 5,000 tonne per day capacity may consume between 2,500 and 4,000 tonnes of refractory material over its operational lifecycle, with lining replacement costs representing a significant fraction of total maintenance expenditure.[36]

The evolution of refractory technology mirrors the development of human civilisation's mastery of fire. Early refractory applications date to antiquity, where clay-based materials lined primitive smelting furnaces and pottery kilns.[3][4] The Industrial Revolution necessitated more durable lining materials capable of sustaining the higher temperatures and greater thermal cycling rates demanded by iron blast furnaces and glass tank furnaces.[2][4] The twentieth century witnessed systematic scientific investigation of refractory compositions and microstructures, culminating in the development of high-alumina, magnesia-chrome, silicon carbide, and zirconia-based refractories.[4][11] Contemporary research has shifted towards optimising monolithic (unshaped) refractories, developing chromium-free alternatives, and integrating computational thermodynamic tools (e.g., FactSage, Thermo-Calc) to predict phase equilibria and corrosion behaviour under specific service environments.[52][35]

1.2 Critical Role of Refractories in Cement and Ceramic Industries (Paraphrased Academic Version)

Refractory materials are fundamental to the operation of high-temperature processing industries, particularly cement, glass, and ceramic manufacturing, where they ensure equipment reliability, thermal efficiency, and product quality under severe service conditions. In the cement industry, the rotary kiln serves as the core unit of clinker production, facilitating the gradual transformation of raw meal into clinker at temperatures reaching approximately 1,400–1,450 °C. The kiln is divided into several operational zones, including the inlet zone, upper and lower transition zones, burning zone, and cooling zone, each characterized by distinct thermal, chemical, and mechanical conditions. Consequently, the refractory lining must be carefully selected to withstand zone-specific challenges such as extreme temperatures, stresses generated by the rotating kiln shell, chemical attack from alkali chlorides, sulfates, and reducing atmospheres, as well as abrasive wear caused by continuous clinker movement. The proper selection and installation of refractory materials are therefore critical for maintaining high kiln availability, minimizing specific energy consumption, ensuring clinker quality, and improving overall plant efficiency and environmental sustainability.

Glass manufacturing furnaces present a different yet equally demanding operating environment. Glass tank furnaces typically function continuously at temperatures between 1,400 and 1,600 °C and are expected to remain operational for service campaigns ranging from 8 to 15 years without major shutdowns. During operation, refractory components such as furnace crowns, sidewalls, throats, and regenerative checkerworks are exposed to corrosive alkali-rich vapours, entrained batch materials, and direct contact with molten glass. These harsh conditions necessitate the use of highly corrosion-resistant refractory materials capable of maintaining structural integrity over prolonged periods. The selection of appropriate refractory systems—such as fused-cast alumina-zirconia-silica (AZS), fused-cast alumina, silica, and basic refractories—for specific furnace areas significantly influences furnace lifespan, thermal efficiency, and glass quality. Inadequate refractory performance can result in erosion, contamination of the glass melt, and the formation of defects that compromise product quality.

The ceramic and advanced ceramics industries further broaden refractory performance requirements. Manufacturing processes frequently involve rapid heating and cooling cycles, making low thermal mass and high thermal shock resistance essential attributes. Refractory kiln furniture and support structures must withstand repeated thermal cycling while maintaining dimensional stability and mechanical strength. Additionally, the production of high-value ceramic and technical ceramic products demands contamination-free refractory materials to prevent undesirable chemical interactions, discoloration, or impurity incorporation into the finished products. As a result, refractories used in ceramic applications must combine excellent thermal stability, chemical inertness, thermal shock resistance, and long-term durability to ensure consistent product quality and manufacturing efficiency.

Overall, refractory materials are indispensable to cement, glass, and ceramic manufacturing processes. Their performance directly affects equipment service life, operational reliability, energy efficiency, product quality, and production costs, making them a key enabling technology for modern high-temperature industries.

2. CLASSIFICATION OF REFRACTORIES

Refractory materials can be classified using several complementary approaches that reflect differences in their chemical composition, microstructure, manufacturing processes, physical characteristics, and intended applications. Owing to the wide variety of refractory products available for diverse industrial environments, no single classification system is sufficient to describe all their properties and performance characteristics. Therefore, international standards and industrial practices commonly adopt multiple classification schemes to provide a comprehensive understanding of refractory behavior under specific service conditions. The major classification categories are discussed in the following sections.

2.1 Classification Based on Chemical Nature

Classification according to chemical nature is one of the most widely used methods for categorizing refractory materials. This approach divides refractories into three principal groups: **acidic, neutral, and basic refractories**. The classification is primarily based on the chemical composition of the refractory and its compatibility with slags, molten materials, and process atmospheres. It is founded on concepts of slag chemistry and oxide acid–base interactions, particularly the Lux–Flood theory that describes acid–base behavior in molten oxide systems.

Acidic refractories are predominantly composed of silica-rich materials, typically containing more than 93% silicon dioxide (SiO_2), along with semi-silica varieties. These refractories are characterized by a high concentration of network-forming oxides, which provide excellent resistance to acidic slags and oxidizing environments. Silica refractories exhibit outstanding dimensional stability at elevated temperatures, particularly after the transformation of quartz into high-temperature phases such as tridymite and cristobalite. Additional advantages include low thermal conductivity, excellent load-bearing capacity at high temperatures, and good resistance to acidic corrosion. However, their performance deteriorates rapidly in the presence of basic slags, alkaline vapors, and calcium-rich compounds because chemical reactions produce low-melting phases that accelerate refractory wear. Consequently, acidic refractories are primarily employed in applications where acidic service conditions prevail, such as glass furnace crowns, coke ovens, and certain ceramic kilns.

Basic refractories consist mainly of magnesia (MgO), dolomite (CaO·MgO), and related compositions that exhibit strong resistance to basic slags and alkaline environments. Their superior chemical compatibility with lime-rich and iron-rich slags makes them indispensable in cement rotary kilns, steelmaking furnaces, and non-ferrous metallurgical operations. Among this category, magnesia-spinel ($MgO–MgAl_2O_4$) refractories have gained widespread acceptance as premium lining materials for cement kiln burning zones due to their excellent thermal stability, clinker coating adherence, corrosion resistance, and thermal shock performance. These materials have largely replaced traditional magnesia-chrome refractories, whose use has declined because of environmental concerns associated with the formation of hazardous hexavalent chromium (Cr^{6+}) compounds during service. The transition to chromium-free refractory systems represents a significant advancement toward safer and more sustainable high-temperature industrial operations.

Neutral refractories, which include alumina, chromite, carbon, silicon carbide, zirconia, and alumina-chromia compositions, possess relatively balanced chemical behavior and can perform effectively in both acidic and basic environments. Their versatility makes them suitable for a broad range of industrial applications where refractory linings are exposed to complex or fluctuating chemical conditions. High-alumina refractories, in particular, are extensively used in cement plants, ceramic kilns, and various metallurgical furnaces owing to their excellent refractoriness, mechanical strength, and resistance to thermal shock and chemical attack.

Overall, classification based on chemical nature provides a practical framework for selecting refractory materials according to the slag chemistry, process atmosphere, and service environment encountered in industrial operations. Proper matching of refractory chemistry with operating conditions is essential for maximizing service life, improving process efficiency, and minimizing maintenance costs.

Neutral refractories, including high-alumina (Al_2O_3 > 45%), chromite, carbon, and silicon carbide, occupy an intermediate position and are resistant to both acidic and basic slags to varying degrees.[2][3] High-alumina refractories are among the most widely deployed in cement preheaters, calciners, and transition zones owing to their combination of refractoriness, thermal shock resistance, and moderate cost.[6][28]

Table 1: Classification of refractories by chemical nature, showing primary oxides, slag compatibility, service temperature ranges, and typical industrial applications.

Type	Primary Oxides	pH Character	Service Temp. (°C)	Key Applications
Acidic	SiO_2 (>93%)	Acidic slags	1500–1700	Glass furnace crowns, coke ovens
Semi-Silica	SiO_2 (70–93%)	Weakly acidic	1400–1650	Glass furnace sidewalls
Neutral – High Alumina	Al_2O_3 (45–99%)	Neutral/amphoteric	1600–1850	Cement kilns, preheaters
Neutral – Chromite	Cr_2O_3–MgO	Neutral	1600–1800	Non-ferrous, cement
Neutral – SiC	SiC (>70%)	Neutral	1400–1750	Cement coolers, incinerators
Basic – Magnesia	MgO (>85%)	Basic	1700–1850	Cement burning zone, EAF
Basic – Dolomite	CaO·MgO	Basic	1700–1800	Steel ladles, cement
Basic – Mag-Chrome	MgO–Cr_2O_3	Basic (legacy)	1700–1850	Cement (legacy), copper smelters
Basic – Mag-Spinel	MgO–$MgAl_2O_4$	Strongly basic	1700–1900	Cement rotary kilns

2.2 Classification by Manufacturing Method

The manufacturing route profoundly influences the microstructure, porosity, phase distribution, and ultimate performance of refractory products.[11][30] Three principal manufacturing pathways are recognised.

Pressed and Fired (Sintered) Refractories: This is the most widely employed manufacturing route for shaped bricks and tiles. Raw materials are blended, milled to controlled particle size distributions (typically following an Andreasen or Dinger-Funk curve to maximise packing density), mixed with temporary binders, uniaxially or isostatically pressed to green densities of 55–70% of theoretical, and fired in tunnel or shuttle kilns at temperatures of 1,400–1,800 °C.[9][30] Sintering promotes grain boundary formation, densification, and the development of secondary phases (e.g., spinel, mullite, forsterite) that critically govern high-temperature mechanical properties.[8][11]

Fused Cast (Electrocast) Refractories: Selected compositions, primarily AZS (Al_2O_3–ZrO_2–SiO_2), high-alumina, and magnesia systems, are arc-melted in electric furnaces at temperatures of 2,000–2,300 °C, poured into sand or ceramic moulds, and directionally solidified.[12][46] The resulting glass-free or low-glass-content microstructure, composed of interlocking crystals of corundum, zirconia, or spinel, confers exceptional corrosion resistance against glass melts and is essentially the only viable option for glass contact zones in float and container glass furnaces.[47][48]

Hand-Moulded and Extruded Refractories: Hand moulding is employed for complex shapes, large slabs, and artisanal production of fireclay products. These methods offer flexibility in shape production but generally result in lower packing density and greater porosity compared to pressing.[30]

2.3 Classification by Physical Form and Shape

Refractories are broadly divided into shaped (preformed) and unshaped (monolithic) categories, a distinction that has become commercially and technically significant over the past four decades as monolithic refractories have captured an increasing share of the market—estimated at 40–55% by volume in developed markets.[2][6]

Shaped refractories include standard bricks (normal, arch, wedge, key, and skewback profiles), special shapes, tiles, and kiln furniture. Standard ISO dimensions allow interchangeable deployment across different kiln systems.[18] Unshaped (monolithic) refractories—castables, ramming mixes, gunning mixes, plastic refractories, mortars, and patching compounds—are installed in situ without the need for high-temperature prefiring, offering significant advantages in terms of joint-free installation, ease of repair, and ability to conform to complex geometries.[6][21] Low-cement castables (LCC), ultra-low-cement castables (ULCC), and no-cement castables (NCC) formulated with microsilica and reactive alumina additions have largely displaced conventional high-cement castables in critical applications owing to their superior hot properties, reduced permeability, and improved corrosion resistance.[21][28]

2.4 Classification by Porosity and Thermal Insulation Function

The porosity of a refractory material—specifically its apparent porosity (AP), total porosity, and pore size distribution—is one of the most critical structural parameters governing thermal conductivity, corrosion resistance, mechanical strength, and permeability to reactive gases and liquids.[11][17]

Dense refractories (AP < 25%, with high-performance grades achieving AP < 10%) are employed in hot-face (lining) positions where direct exposure to high temperatures, slag, or glass melt occurs. Low apparent porosity minimises infiltration of corrosive liquids and gases into the brick structure, reducing the depth of chemical attack.[1][2] For cement kiln burning zone bricks, target AP values of 12–18% are typical for magnesia-spinel bricks, representing a compromise between corrosion resistance and thermal shock resistance.[8][53]

Insulating refractories (AP 45–85%) are utilised as backup lining or standalone thermal insulation to reduce heat losses through kiln shells, furnace walls, and roofs.[1][2] They include insulating firebricks (IFB), calcium silicate boards, microporous silica panels, ceramic fibre products (blankets, boards, modules), and lightweight castables.

Table 2. Classification of refractories by porosity and thermal insulation function, showing key physical properties and industrial applications.

Category	Apparent Porosity (%)	Bulk Density (g/cm³)	Thermal Cond. (W/m·K at 1000°C)	Applications
Dense (hot face)	10–20	2.8–3.5	2.0–6.0	Kiln linings, furnace hot face
Semi-dense	20–30	2.3–2.8	1.0–2.5	Backup lining
Insulating IFB K23	50–65	0.8–1.0	0.25–0.35	Kiln backup, preheater insulation
Insulating IFB K26	45–60	0.9–1.1	0.35–0.55	Furnace roofs, sidewalls
Ceramic Fibre	80–95	0.08–0.20	0.10–0.25	Expansion joints, door seals

Category	Apparent Porosity (%)	Bulk Density (g/cm³)	Thermal Cond. (W/m·K at 1000°C)	Applications
Blanket				
Microporous Silica Panel	85–95	0.15–0.35	0.02–0.04 (200°C)	Ultra-insulation, kiln door
Calcium Silicate Board	75–90	0.25–0.40	0.08–0.12	Preheater, calciner insulation

2.5 Classification by Heat Duty (Service Temperature)

Heat duty classification provides a practical guide to the maximum service temperature of a refractory material under specific load and atmospheric conditions. The **Pyrometric Cone Equivalent (PCE) test** was traditionally used to classify refractories according to their heat resistance. In this test, a small cone made from the refractory material is heated alongside standard reference cones. The temperature at which the test cone bends or deforms is compared with the reference cones to determine its refractoriness.

However, the PCE test only indicates the temperature at which a material begins to soften and does not accurately represent actual industrial operating conditions. Therefore, modern refractory evaluation mainly relies on the **Refractoriness Under Load (RUL) test**, which measures the material's ability to withstand high temperatures while carrying a load, and the **Creep in Compression test**, which evaluates its resistance to slow deformation during prolonged exposure to heat and stress.

Table 3 Presents the heat-duty classification of refractories, including their typical service temperature ranges, corresponding PCE values, common refractory types, and their applications in various zones of cement and glass manufacturing industries.

Heat Duty Class	Service Temp. (°C)	PCE Range	Typical Materials	Industrial Zone Examples
Super Duty	>1650	33–38+	Fused mullite, high-Al_2O_3	Glass furnace crown
High Duty	1500–1650	30–33	High alumina (70–99%), mag-spinel	Cement burning zone
Intermediate Duty	1350–1500	27–30	Fireclay (45–70% Al_2O_3)	Cement upper transition
Low Duty	1150–1350	23–27	Fireclay, semi-silica	Preheater cyclones

Heat Duty Class	Service Temp. (°C)	PCE Range	Typical Materials	Industrial Zone Examples
Insulating / Low Temp	<1150	<23	Insulating firebricks, boards	Kiln backup, shell insulation

2.6 Classification by Main Constituent and Purity

Advanced refractory applications, including technical ceramics, laboratory equipment, and specialty glass furnaces, demand materials with exceptionally high chemical purity. Trace impurities such as Fe_2O_3, TiO_2, CaO, and Na_2O can significantly reduce refractoriness, creep resistance, and color stability. Therefore, high-purity materials such as **α-alumina (>99.5% Al_2O_3)**, **magnesia (>99% MgO)**, and **tabular alumina** are widely used in these applications. According to **ISO 10081**, dense shaped refractories are classified primarily based on their content of major constituents such as Al_2O_3, MgO, SiC, C, ZrO_2, and Cr_2O_3.

2.7 Special Refractories

Special refractories comprise advanced materials developed for applications requiring exceptional performance beyond conventional refractory classifications. These materials are typically characterised by ultra-high temperature resistance (>2,000 °C), superior chemical stability, or the ability to operate under severe combined thermal, mechanical, and chemical conditions. Zirconia (ZrO_2) refractories are among the most important special refractories due to their extremely high melting point (2,715 °C), low thermal conductivity, and excellent resistance to molten-glass corrosion. Consequently, they are extensively used in glass furnace throat blocks, electrode assemblies, and other critical high-temperature zones. To prevent the damaging tetragonal-to-monoclinic phase transformation near 1,170 °C, zirconia is stabilised using additives such as CaO, MgO, or Y_2O_3, which enhance its thermal and structural stability during service.

Carbon and graphite refractories derive their superior performance from the unique properties of carbon, including high thermal conductivity, low thermal expansion, and exceptional resistance to thermal shock. These materials are widely used in blast furnace hearths, aluminium electrolysis cells, and Acheson furnaces, where severe thermal conditions exist. However, their application is limited by their tendency to oxidise in air at temperatures above 400–500 °C. Consequently, protective coatings, antioxidant treatments, or reducing atmospheres are often required to minimize oxidation and prolong service life.

3. CLASSIFICATION BASED ON MAIN CHEMICAL COMPOSITION

3.1 Silica Refractories

Silica refractories (SiO_2 > 93%) are manufactured from quartzite, ganister, or high-purity quartz sands with small additions of lime (1–3% CaO) to facilitate the formation of tridymite and cristobalite during firing. The transformation of quartz to tridymite and cristobalite involves substantial irreversible volume changes, requiring carefully controlled heating schedules during the commissioning of silica brick linings. Once fully converted, silica refractories exhibit minimal thermal expansion above 600 °C and excellent dimensional stability at elevated temperatures. These properties, combined with their resistance to silica-rich glass melts and low contamination potential, make them widely used in glass furnace crowns and superstructures. However, their service life can be limited by lime-induced corrosion and alkali-vapour-driven devitrification processes.

3.2 Fireclay Refractories

Fireclay refractories are alumina–silica-based materials containing approximately **25–45% Al_2O_3** and represent one of the most widely produced refractory categories. They are manufactured from kaolinite-rich clays that, upon firing, transform into metakaolin and subsequently develop a microstructure composed of **mullite crystals embedded within a siliceous glass matrix**. The mullite-to-glass ratio significantly influences refractoriness, hot strength, and thermal shock resistance. Due to their moderate service temperature range (1,300–1,500 °C), good resistance to thermal cycling, and relatively low cost, fireclay bricks are widely employed in cement plant preheaters, calciners, and kiln inlet linings.

3.3 High-Alumina Refractories

High-alumina refractories, containing approximately **45–99% Al_2O_3**, constitute one of the most important and compositionally diverse classes of refractory materials. Increasing alumina content generally enhances refractoriness, hot strength, corrosion resistance, and high-temperature stability. Owing to their excellent balance of thermal, mechanical, and chemical properties, these refractories are extensively employed in cement kilns, ceramic kilns, glass furnaces, and other high-temperature industrial applications. Their versatility and superior performance make them a cornerstone of modern refractory technology.

Commercial grades are designated by alumina content: 50%, 60%, 70%, 80%, 90%, and >99% (corundum). The key phase assemblages are mullite (for compositions below ~72% Al_2O_3), corundum + mullite (72–100% Al_2O_3), and pure corundum at ≥99% Al_2O_3.

Increasing Al_2O_3 content progressively improves: maximum service temperature (from ~1,500 °C for 50% Al_2O_3 grades to >1,850 °C for corundum bricks); load-bearing capacity (measured by RUL test); and resistance to acidic and mildly basic slag attack.[6][28] The transition from fireclay to high-alumina bricks for cement kiln transition zones is justified by the substantially higher alkali resistance of corundum-mullite assemblages compared to glass-rich fireclay microstructures.[5]

Table 4. Properties of high-alumina refractories as a function of Al_2O_3 content, showing phase assemblage, service temperature, and key mechanical/physical properties.

Al_2O_3 Content (%)	Phase Assemblage	T_service (°C)	RUL $T_{0.5}$ (°C)	CCS (MPa)	AP (%)	Key Applications
45–50	Mullite + glass	1300–1450	1250–1350	40–60	18–25	Preheater, calciner
60	Mullite + minor corundum + glass	1400–1550	1350–1450	50–80	16–22	Upper transition zone
70	Mullite-rich + corundum	1500–1620	1420–1500	60–100	14–20	Lower transition zone
80	Corundum + mullite	1600–1750	1500–1580	80–130	12–18	Cooling zone, calciner
90	Corundum dominant	1700–1800	1550–1620	100–160	10–16	High-stress kiln zones
>99 (Tabular)	α-Al_2O_3 only	1800–1850+	1620–1700	120–200	8–14	Slide gate, ladle, specialty

3.4 Magnesia and Magnesia-Spinel Refractories

Magnesia refractories (MgO > 85%) are derived from natural magnesite ($MgCO_3$) calcined and dead-burned at temperatures of 1,600–1,800 °C to produce periclase (MgO) grains of controlled purity and crystal size.[2][8] Dead-burned magnesia (DBM) and sea-water magnesia (fused magnesia from seawater precipitation) constitute the two principal raw material sources, differing in purity (Fe_2O_3, CaO, SiO_2 impurity levels) and crystal size (typically 50–200 μm for DBM, 500–2,000 μm for fused magnesia).[8]

The introduction of $MgAl_2O_4$ spinel (either pre-formed or in-situ generated from Al_2O_3 additions reacting with periclase during service) profoundly improves thermal shock resistance relative to pure magnesia by creating a microstructure in which controlled microcracking around spinel inclusions dissipates thermal stress energy.[53][50] This mechanism, combined with the high melting point of spinel (2,135 °C) and its chemical stability within the cement kiln environment, has established magnesia-spinel bricks as the dominant lining material for the burning zone of rotary cement kilns worldwide, accounting for approximately 60–75% of burning zone consumption by volume.[23][52]

The **CaO/SiO_2 (C/S) ratio** is a key quality parameter in magnesia refractories, as it governs the formation of high-temperature mineral phases. A C/S ratio above 2 promotes the formation of high-melting compounds such as **C_2S** and **C_3S**, while suppressing low-melting phases including **merwinite** and **monticellite**, which adversely affect hot mechanical properties. Consequently, premium magnesia-spinel refractories for cement rotary kilns are typically manufactured with C/S ratios ranging from **2.0 to 3.5** to ensure superior high-temperature stability and strength.

The development of **chromium-free magnesia refractories** has emerged as a major research focus due to environmental concerns associated with hexavalent chromium formation in magnesia-chrome bricks. Alternative phase assemblages based on **hercynite, galaxite, and periclase–calcium zirconate** have demonstrated comparable thermal shock resistance and clinker coating adherence while offering improved environmental compatibility and operational safety.

3.5 Silicon Carbide Refractories

Silicon carbide (SiC) refractories occupy a unique niche in the refractory landscape by virtue of their exceptionally high thermal conductivity (15–40 $W \cdot m^{-1} \cdot K^{-1}$ compared to 2–6 $W \cdot m^{-1} \cdot K^{-1}$ for alumina bricks), outstanding abrasion resistance, high thermal shock resistance, and moderate chemical resistance.[2][17] Four commercial bonding systems are employed: oxide-bonded, nitride-bonded (Si_3N_4), oxynitride-bonded (sialon), and self-bonded/recrystallised SiC.

In the cement industry, SiC bricks and castables are principally applied in clinker coolers where high abrasion from moving clinker granules combined with rapid thermal cycling creates conditions that rapidly destroy conventional alumina products.[36] The abrasion resistance of SiC (hardness ~9.3 Mohs) is approximately 3–5 times superior to that of 70% alumina bricks under equivalent test conditions.[2] SiC-based refractories are also used in preheater cyclone cone sections, riser ducts, and kiln inlet sections where alkali-rich gases and high-velocity particle-laden flows cause simultaneous chemical and erosive attack.[5][36]

3.6 Zirconia and Zircon Refractories

Zirconium silicate ($ZrSiO_4$, zircon) refractories are distinguished by their exceptional resistance to glass melt corrosion—the key property that determines service life in glass tank bottom blocks, paving bricks, and throat tiles.[12][46] The mechanism of zircon's stability in glass melts involves the formation of a thin protective ZrO_2 layer at the glass-refractory interface that significantly retards further dissolution.[48] Zircon also offers low, consistent thermal expansion ($\alpha = 4.2 \times 10^{-6}\ K^{-1}$) and good load-bearing capacity up to ~1,500 °C (above which zircon dissociates to $ZrO_2 + SiO_2$).[2]

Pure zirconia (ZrO_2) refractories, particularly in its partially stabilised (PSZ) and tetragonal polycrystalline (TZP) forms, achieve the highest service temperatures of any commercially used oxide refractory.[35][54] ZrO_2 additions to magnesia-spinel matrices introduce transformation-toughening via the stress-induced t→m ZrO_2 phase change, delivering fracture toughness improvements of 40–60% over base magnesia-spinel and extending campaign life in cement kiln burning and transition zones where clinker-melt corrosion is compounded by shell ovality stresses.[54]

4. PHYSICOCHEMICAL AND THERMO-MECHANICAL PROPERTIES

4.1 Physical Properties

4.1.1 Apparent Porosity and Bulk Density

Apparent porosity (AP) and bulk density (BD) are the most universally measured physical properties of refractories, governed by ISO 5017 (vacuum and boiling water method) and equivalent ASTM C20 and C830 standards.[18][20] AP represents the percentage of open (interconnected) pore volume relative to the external volume of the specimen; it excludes sealed (closed) pores that are inaccessible to the immersion liquid.[11] Understanding these relationships is critical because AP directly governs the rate of slag or glass infiltration into the brick structure, which is the initiating mechanism for most refractory corrosion scenarios.

4.1.2 Specific Gravity and Firing Shrinkage

Specific gravity (or true density) is the ratio of the mass of a material to the mass of an equal volume of water, measured on a finely powdered sample from which all pores have been evacuated.[18] Firing shrinkage (permanent linear change on reheating, PLCR) quantifies the dimensional change of a refractory specimen upon re-heating to a specified temperature and is critical for predicting lining stability and joint opening or closing behaviour in service.[2]

Table 5. Representative physical properties of major refractory types (typical commercial product ranges).

Refractory Type	Bulk Density (g/cm^3)	Apparent Porosity (%)	Specific Gravity (g/cm^3)	Cold Crushing Strength (MPa)
Silica (>93% SiO_2)	1.75–1.90	18–25	2.32–2.35	25–55
Fireclay (45% Al_2O_3)	1.90–2.20	18–26	2.55–2.65	30–60
High Alumina 70%	2.30–2.60	14–22	3.00–3.15	60–110
High Alumina 90%	2.65–2.90	10–18	3.60–3.75	100–170
Magnesia (DBM)	2.80–3.00	14–20	3.55–3.60	60–100
Magnesia-Spinel	2.85–3.05	12–18	3.50–3.60	70–120
Zircon	3.50–3.80	12–20	4.60–4.65	100–180
AZS (33% ZrO_2)	3.50–3.80	1–3	3.80–3.90	200–350
SiC (oxide-bonded)	2.50–2.65	14–20	3.20–3.25	80–140

4.2 Mechanical Properties

4.2.1 Cold Crushing Strength

Cold crushing strength (CCS), measured per ISO 8895 or ASTM C133, quantifies the compressive load-bearing capacity of a refractory at ambient temperature and represents the most widely reported mechanical property.[18][20] CCS values are sensitive to microstructural parameters including grain size, grain bonding, porosity, and matrix composition. While CCS does not directly predict hot mechanical behaviour, it serves as a quality control indicator of sintering completeness and brick uniformity.[11] Typical CCS requirements for cement kiln burning zone bricks are >60–80 MPa; for high-stress applications such as working linings in steel ladles, values of >150 MPa may be specified.

4.2.2 Cold Modulus of Rupture (CMOR)

The cold modulus of rupture (CMOR, ISO 5014 or ASTM C133) is a three-point bend test that measures the flexural strength of a refractory bar specimen at ambient temperature.[18][20] CMOR is particularly relevant for refractory precast shapes, kiln furniture, and castable linings that experience bending loads during installation or in service. High-performance tabular alumina castables commonly exhibit cold modulus of rupture (CMOR) values of approximately 15–25 MPa at room temperature. At elevated service temperatures, the softening of the bonding matrix results in a reduction in bending strength, with CMOR values typically decreasing to 5–15 MPa. Nevertheless, these castables maintain adequate mechanical integrity for demanding high-temperature applications in cement, steel, and ceramic industries.

4.2.3 Abrasion Resistance

Abrasion resistance is a critical performance parameter for refractories operating in high-wear environments involving moving bulk materials or particle-laden gas streams. Applications such as cement kiln cooler grates, preheater cyclones, riser ducts, and calciner outlets subject refractory linings to severe erosive and abrasive conditions. Consequently, refractory materials with high wear resistance are essential for minimizing lining degradation, extending service life, and ensuring reliable plant operation.

The standard test (ISO 10059 or ASTM C704) employs a sand-blast abrasion apparatus to measure material loss in cm^3 under standardised impingement conditions. SiC-based refractories typically show losses of 2–6 cm^3, compared to 8–20 cm^3 for 70% alumina bricks and >25 cm^3 for fireclay bricks under the same test conditions.[20]

4.3 Thermal Properties

4.3.1 Thermal Conductivity

Thermal conductivity (λ) is a critical design parameter for both heat transfer modelling of industrial furnaces and for assessing the thermal protection provided to kiln shells and furnace casings.[1][2] For dense refractory bricks, λ is governed by phonon conduction through the solid phases and, at elevated temperatures, by radiative transfer through pores and grain boundaries.[11] Magnesia refractories exhibit the highest thermal conductivity of common oxide refractories (3–6 $W\cdot m^{-1}\cdot K^{-1}$ at 1,000 °C), followed by high-alumina (2–4 $W\cdot m^{-1}\cdot K^{-1}$), fireclay (1–1.5 $W\cdot m^{-1}\cdot K^{-1}$), and silica (1–1.5 $W\cdot m^{-1}\cdot K^{-1}$). SiC refractories far exceed all oxide materials, with λ = 15–40 $W\cdot m^{-1}\cdot K^{-1}$ depending on bonding system and SiC content.[2][17]

4.3.2 Thermal Shock Resistance

Thermal shock resistance (TSR) is the ability of a refractory to withstand rapid temperature changes without catastrophic cracking or spalling. It is governed by the ratio of thermal stress generated (proportional to $E\cdot\alpha\cdot\Delta T$, where E = Young's modulus, α = thermal expansion coefficient, ΔT = temperature differential) to the material's fracture resistance.[49] A comprehensive review by Meng et al. (2024) confirmed that the coefficient of thermal expansion (CTE) is the most critical single factor governing thermal shock resistance index across the full range of ceramics from porcelain to advanced structural refractories, with porosity and fracture toughness also making significant quantitative contributions.[49] Materials with low E·α products (e.g., cordierite; silicon carbide, where high conductivity rapidly equilibrates temperature gradients) or high fracture toughness K_Ic (e.g., TZP zirconia: K_Ic = 10–12 MPa·m^0.5 from transformation toughening) exhibit superior TSR.[49][54]

Standard TSR tests include the water-quench method (ISO 2477: repeated cycling between a specified temperature—typically 950°C for fireclay grades—and room-temperature water), and the small prism method (EN 993-11: measuring strength retention after a specified number of thermal cycles).[18] Magnesia-spinel bricks achieve 25–50 water-quench cycles before strength loss exceeds 30%, compared to 5–15 cycles for pure magnesia bricks of equivalent composition, quantitatively demonstrating the TSR benefit of microcrack-toughening by spinel inclusions.[53][50] In-situ spinel formation in $MgAl_2O_4$-containing alumina castables improves thermal shock resistance through controlled microcracking around spinel inclusions, with quantitative data on RUL and HMOR confirming the beneficial effect as a function of spinel content.[53]

The role of h-BN composite powder additions in Al_2O_3–C refractories has been demonstrated to enhance thermal shock resistance through in-situ formation of spinel ($MgAl_2O_4$) and AlN whiskers that deflect and branch crack propagation, demonstrating the universality of the spinel microcrack-toughening mechanism under combined thermal shock and slag corrosion conditions relevant to cement kiln and steel ladle service.[50]

4.4 Thermo-Mechanical Properties

4.4.1 Refractoriness Under Load (RUL)

Refractoriness under load (RUL), measured per ISO 1893 or ASTM C16, determines the temperature at which a cylindrical refractory specimen under a fixed compressive stress of 0.2 MPa exhibits defined deformation endpoints: typically $T_{0.5}$ (temperature at 0.5% compression from the original length at 600 °C) and $T_{2.0}$ (temperature at 2.0% compression).[19][18] RUL is arguably the most important single mechanical property for kiln and furnace design, since it directly limits the maximum operating temperature at which a refractory can support the weight of overlying structure or the load imposed by kiln shell ovality.

4.4.2 Creep in Compression

Creep in compression measures the time-dependent deformation of a refractory specimen under constant compressive load at a fixed high temperature (ISO 3187 Unlike the Refractoriness Under Load (RUL) test, which evaluates deformation during continuous heating, the creep in compression test assesses the long-term dimensional stability of a refractory under a constant load and temperature. This test more accurately simulates actual service conditions encountered in industrial furnaces and kilns. Excessive creep can result in joint closure, roof distortion, and shell deformation, ultimately compromising structural integrity. Improving creep resistance typically involves minimizing the glassy phase content, as these phases undergo viscous flow at elevated temperatures and contribute significantly to long-term deformation.

4.4.3 Hot Modulus of Rupture (HMOR)

The Hot Modulus of Rupture (HMOR), determined according to ISO 5013 or ASTM C583, measures the flexural strength of refractory materials at elevated temperatures, typically between 1,000 and 1,400 °C. Unlike the Cold Modulus of Rupture (CMOR), HMOR assesses the integrity of the refractory bonding system under actual service conditions. Its value is significantly influenced by the viscosity and stability of the glassy matrix at high temperatures. Refractories containing mullite-rich microstructures, particularly high-alumina compositions, generally demonstrate higher HMOR values than glass-rich materials because mullite retains substantial mechanical strength at temperatures approaching 1,600 °C.

Table 6. Table 6. Key thermo-mechanical properties and test standards for major refractory types (indicative commercial product ranges) [2, 6, 17, 20, 53].

Property	Test Standard	Unit	Fireclay 45%	High Al_2O_3 70%	Mag-Spinel	AZS 33% ZrO_2	SiC (nitride-bonded)
CCS	ISO 8895	MPa	35–55	60–110	70–120	250–350	100–150
CMOR	ISO 5014	MPa	5–10	8–15	10–18	30–45	25–40
HMOR at 1400°C	ISO 5013	MPa	2–5	5–12	8–14	12–25	20–35
RUL $T_{0.5}$	ISO 1893	°C	1250–1350	1400–1500	1550–1650	>1700	1550–1650
Creep at 1400°C/2h	ISO 3187	%	0.5–2.0	0.2–0.8	0.2–0.5	<0.2	0.1–0.4
Thermal	ISO 8894	W/m·K	1.0–1.5	2.0–4.0	3.0–5.0	2.5–4.0	15–25

Property	Test Standard	Unit	Fireclay 45%	High Al_2O_3 70%	Mag-Spinel	AZS 33% ZrO_2	SiC (nitride-bonded)
Conductivity		at 1000°C					

4.5 Corrosion and Chemical Resistance

4.5.1 Slag and Glass Melt Corrosion

Corrosion by molten slag (in cement kilns) and glass melt (in glass furnaces) is the dominant degradation mechanism limiting refractory campaign life in both industries.[5][12] The corrosion process involves three sequential steps: (i) dissolution of the refractory surface into the melt (dissolution rate controlled by the thermodynamic driving force); (ii) diffusion of dissolved species away from the interface into the bulk melt; and (iii) penetration of the melt into the brick microstructure along pores and grain boundaries, creating a reaction zone of altered composition and modified mechanical properties.[12][47] At the AZS–glass melt interface, an Al_2O_3- and SiO_2-enriched viscous layer forms that saturates the melt in alumina, thereby reducing ZrO_2 solubility; this mechanism, combined with a dense microstructure and low closed porosity, accounts for the exceptional corrosion resistance of fused cast AZS relative to sintered alumina grades.[48]

Static corrosion tests of AZS grades in barium crystal glass at 1,480 °C have shown that corrosion depth varied significantly among AZS grades; SEM-EDS confirmed dissolution of the silica-rich vitreous matrix, alkali enrichment, and formation of protective needle-like corundum crystals, while baddeleyite dendrites demonstrated superior corrosion resistance.[47] AZS refractory quality cannot be adequately judged from ZrO_2 content and density alone; the chemical composition and behaviour of the glassy phase—specifically its exudation onset temperature (optimal: above 1,400 °C) and volume fraction (optimal: 2–3% melt-out)—are decisive quality parameters, achieved through oxidative melting and <0.30% total impurities.[46]

4.5.2 Alkali Attack and CO Disintegration

Alkali vapour attack (K_2O, Na_2O, K_2SO_4, KCl, NaCl) is a pervasive degradation mechanism in cement preheaters and lower transition kilns. Alkali-induced degradation is a major failure mechanism in cement kiln refractories. Alkali vapours condense within the temperature range of 700–900 °C, penetrate the refractory pore structure, and react with alumino-silicate phases to form expansive compounds such as leucite and kalsilite. The associated volume expansion generates internal stresses that promote cracking and spalling. Consequently, high-alumina corundum–mullite refractories with low silica and glass-phase contents exhibit significantly greater alkali resistance than conventional fireclay materials.

Fireclay refractories are also susceptible to carbon monoxide disintegration, which occurs through the Boudouard reaction ($2CO \rightarrow CO_2 + C$) catalyzed by iron-containing phases. Carbon deposition within the pore network causes swelling, cracking, and eventual structural failure. The incorporation of TiO_2 additives is a well-established mitigation strategy, as titanium forms stable iron titanate phases that reduce the catalytic activity of iron and thereby limit carbon deposition.

5. SPECIAL REFRACTORIES

5.1 Fused Cast Refractories and AZS Systems

Fused-cast refractories are considered the highest-performance refractory materials for applications involving direct contact with molten glass. Their excellent corrosion resistance is primarily due to their very low open porosity (typically 0.5–3% for AZS refractories) and highly uniform microstructure, which prevent glass penetration and chemical attack more effectively than conventional sintered refractories.

These refractories are produced by melting carefully selected raw materials in an electric arc furnace at temperatures ranging from 2,000 to 2,300 °C. The molten material is then cast into specially prepared moulds, typically made from sand or zirconia-based materials, and subsequently annealed under controlled conditions to relieve internal thermal stresses and ensure structural stability.

Among fused-cast refractories, alumina-zirconia-silica (AZS) materials are the most widely used in glass tank furnaces. They are commercially available in three common grades:

AZS-33 (~33% ZrO_2)

AZS-36 (~36% ZrO_2)

AZS-41 (~41% ZrO_2)

The microstructure of AZS refractories consists mainly of corundum (α-Al_2O_3) crystals, baddeleyite (ZrO_2) grains, and a surrounding glassy phase. As the zirconia content increases, the amount of glassy phase decreases, resulting in improved resistance to corrosion by sodium-rich molten glass. Therefore, AZS-41 generally provides better corrosion resistance and longer service life than AZS-33, especially in the most aggressive glass-contact regions.

Table 7 summarizes the key properties of fused-cast refractory products, including AZS grades, fused alumina, and fused zirconia refractories, commonly used in glass tank furnaces and other severe high-temperature applications.

Grade	Al_2O_3 (%)	ZrO_2 (%)	SiO_2 (%)	Glass Phase (%)	BD (g/cm³)	AP (%)	CCS (MPa)	Corrosion Resistance
AZS-33	50–52	32–34	13–15	20–25	3.50–3.65	1.5–3.0	250–300	Good
AZS-36	47–50	35–37	12–14	16–20	3.60–3.75	1.0–2.5	280–340	Very Good
AZS-41	44–47	40–42	11–14	10–15	3.75–3.90	0.5–2.0	300–380	Excellent
Fused Al_2O_3 (β)	93–95	—	4–6	5–10	3.30–3.50	2.0–4.0	200–280	Good
Fused Zirconia	—	93–95	3–5	3–8	5.00–5.20	1.0–3.0	300–400	Excellent

5.2 Zircon and Zirconia Refractories

Zircon refractories are intermediate-performance materials that offer better corrosion resistance than conventional high-alumina refractories while being less expensive than fully stabilized zirconia products. They are particularly valued in glass-contact applications where a balance between performance and cost is required.

Sintered zircon bricks typically contain more than **60% zircon ($ZrSiO_4$)** and are manufactured using zircon flour and zircon sand. The raw materials are pressed into shape and fired at temperatures between **1,600 and 1,650 °C**. Careful control of the firing temperature is essential. If the temperature is too low, complete zircon formation is not achieved, whereas excessively high temperatures can cause zircon to decompose into **zirconia (ZrO_2)** and **silica (SiO_2)**. This decomposition reduces the excellent corrosion resistance that makes zircon refractories attractive for glass furnace applications.

For the most demanding service conditions, **yttria-stabilized zirconia (YSZ)** refractories are considered among the highest-performance refractory materials available. These materials contain approximately **3–8 mol% yttria (Y_2O_3)**, which stabilizes the zirconia crystal structure and prevents damaging phase transformations. YSZ refractories exhibit exceptional resistance to corrosion by aggressive glass melts, including fluoride-containing, optical, and borosilicate glasses.

A major advantage of YSZ is its outstanding mechanical toughness. In the **tetragonal zirconia polycrystal (3Y-TZP)** form, fracture toughness values can reach **10–12 MPa·m$^{1/2}$**, significantly higher than those of most conventional ceramic materials. As a result, YSZ refractories can maintain their structural integrity even after prolonged exposure to severe glass-melting environments at temperatures of **1,600–1,700 °C**, making them ideal for critical glass-contact components and high-temperature specialty applications.

5.3 Carbon and Graphite Refractories

Carbon refractories include a wide range of materials such as **carbon bricks, graphite blocks, carbon ramming masses, and carbon–silicon carbide (C–SiC) composites**. These refractories are valued for the unique properties of carbon, which make them highly effective in severe high-temperature environments.

One of their most important characteristics is their **high thermal conductivity**, which can range from approximately **5 to 150 W·m^{-1}·K^{-1}**, depending on the degree of graphitization. This allows heat to be transferred efficiently through the material, reducing thermal gradients and the risk of thermal stress. Graphite also exhibits **very low thermal expansion**, including negative thermal expansion in certain crystallographic directions, which contributes to excellent dimensional stability during heating and cooling cycles.

Another major advantage of carbon refractories is their **exceptional thermal shock resistance**. Unlike most oxide-based refractories, carbon materials can withstand rapid temperature fluctuations without cracking or spalling. This combination of high thermal conductivity, low thermal expansion, and superior thermal shock resistance makes carbon refractories particularly suitable for demanding applications such as blast furnace hearths, aluminium reduction cells, ladles, and other high-temperature metallurgical processes.

6. INSULATING REFRACTORIES AND FIREBRICKS

Insulating refractories fulfil the complementary function to dense hot-face materials in industrial furnace systems: they minimise heat losses through the furnace structure, maintain acceptable outer surface temperatures for personnel safety, reduce kiln shell temperature to protect the steel structure, and improve the overall energy efficiency of high-temperature processes.[33] In a cement kiln with a 5-m shell diameter and 80-m total length, reducing average outer shell temperature from 250 °C to 200 °C saves approximately 500 kW of radiated and convected heat, equivalent to roughly 3,600 GJ annually at full capacity.

6.1 Insulating Firebricks (IFB)

Insulating firebricks are manufactured by three principal processes that introduce controlled high porosity: (i) burnout of organic pore-forming agents (sawdust, polystyrene beads, expanded perlite) during firing; (ii) foaming of a slurry with chemical blowing agents followed by casting and drying; and (iii) direct forming of calcined aggregate-free lightweight raw materials (diatomite, vermiculite, perlite).[2] IFB are classified by maximum service temperature into grades K20 (1000°C), K23 (1150°C), K26 (1300°C), K28 (1400°C), and K30 (1500°C), following ASTM C155 nomenclature.[20]

A combined lining of 150 mm dense high-alumina brick (hot face) + 75 mm K26 IFB (insulating backup) + 20 mm calcium silicate board reduces kiln shell temperature by 80–120 °C compared to the equivalent dense brick-only design of the same total thickness, with a payback period typically below 18 months at current energy costs.

6.2 Ceramic Fibre Products

Refractory ceramic fibre (RCF) products—manufactured by spinning or blowing molten alumino-silicate compositions (47–60% Al_2O_3) into continuous or staple fibres—offer the lowest thermal mass of any refractory product category, enabling rapid furnace heat-up and cool-down cycles that dramatically reduce energy consumption in batch-fired ceramic kilns. The occupational health concerns associated with RCF (WHO Group 2B carcinogen classification for certain alumino-silicate fibres) have stimulated the development of bio-soluble fibre alternatives (calcium-magnesium-silicate (CMS) fibres, calcium-aluminium-silicate (CAS) fibres) that dissolve in physiological fluids and do not persist in lung tissue.[2][17]

Table 8. **Properties of insulating refractory and fibre products, classified by service temperature, thermal conductivity, and bio-solubility.**

Product	Classification Temp. (°C)	BD (kg/m³)	λ at 800°C (W/m·K)	Specific Heat (kJ/kg·K)	Bio-soluble
RCF Blanket (Al-Si)	1260	96–128	0.22–0.28	1.05–1.10	No (Group 2B)
High-Al Fibre Blanket	1400	128–160	0.25–0.35	1.00–1.05	No
Polycrystalline Mullite	1600	160–200	0.30–0.45	0.95–1.00	No
CMS Bio-Soluble Fibre	1000	96–128	0.22–0.30	1.00–1.08	Yes

Product	Classification Temp. (°C)	BD (kg/m³)	λ at 800°C (W/m·K)	Specific Heat (kJ/kg·K)	Bio-soluble
Microporous Silica	1000	250–300	0.020–0.035	0.90–1.00	N/A
Calcium Silicate Board	950	200–350	0.08–0.12	0.85–0.95	N/A
IFB K26	1300	600–800	0.35–0.45	0.90–1.00	N/A

7. SILICA AND MULLITE REFRACTORIES

7.1 Silica Refractories: Phase Chemistry and Applications

The SiO_2 phase diagram presents a rich polymorphic landscape critical to understanding the service behaviour of silica refractories. The target microstructure for commercial silica bricks consists of approximately 50–70% cristobalite + 25–40% tridymite + <5% residual quartz, since quartz retains the largest specific volume change at 573°C (α-β quartz inversion, ~1.5% volume change) and is therefore the most damaging polymorph for thermal shock behaviour.[11][2]

The lime mineraliser added during batch preparation (CaO = 1.5–3.5%) serves two functions: suppressing the thermodynamic stability field of quartz relative to tridymite and cristobalite, and providing a low-viscosity liquid film that accelerates grain boundary diffusion and densification. The characteristic microstructure of well-fired silica brick consists of an interlocking framework of bladed tridymite and granular cristobalite in a minimal residual glassy matrix of lime-silicate composition.[11]

In glass furnace crown applications, silica refractories must sustain continuous structural loads at 1,600–1,650°C for 8–12 year campaigns while resisting attack by sodium and potassium vapours from the glass batch.[12] The corrosion mechanism involves condensation of alkaline vapours in the cool exterior of the crown, penetration to the hot face, reaction with SiO_2 to form sodium/potassium silicate melts of low viscosity, and progressive fluxing of the brick microstructure. Campaign life is significantly influenced by furnace atmosphere control, particularly the reduction of Na_2O and K_2O vapour partial pressures through batch composition optimisation.

7.2 Mullite Refractories

Mullite ($3Al_2O_3{\cdot}2SiO_2$, Al_2O_3 content ≈ 71.8 wt%) is the thermodynamically stable phase at high temperature in the Al_2O_3–SiO_2 binary system between approximately 60 and 100% Al_2O_3.[31] It is distinguished by an exceptional combination of properties: high melting point (1,890°C congruent melting), low thermal expansion coefficient ($\alpha = 4–6 \times 10^{-6}\ K^{-1}$), good thermal shock resistance, excellent creep resistance due to its chain silicate structure and strong Si–O–Al bonding, and chemical stability against both acidic and mildly basic environments. Mullite refractories are manufactured from natural and synthetic raw materials: kyanite, sillimanite, or andalusite ($AlSiO_5$ polymorphs that convert to mullite + SiO_2 on firing at 1,350–1,550°C); co-sintered alumina-silica mixes of controlled stoichiometry; electrofused mullite from arc-melted compositions; and gel-derived sol-gel mullite for ultra-high-purity applications.[31][11] Applications in cement and ceramic industries include cement kiln transition zone and inlet cone linings, kiln furniture for firing electronic ceramics, and glass furnace regenerator checker bricks where mullite's resistance to sulphate and alkali condensate attack significantly extends service life compared to fireclay alternatives.[31][36]

8. MONOLITHIC REFRACTORIES AND ACCESSORIES

8.1 Castable Refractories

Castable refractories are monolithic refractory materials consisting of refractory aggregates, fine fillers, and hydraulic or chemical binders. These materials are mixed with water at the installation site and subsequently placed by casting, pouring, pumping, or vibration into the desired configuration. After curing to develop initial mechanical strength, the castable lining undergoes controlled drying and heating to achieve its final refractory properties. Owing to their installation flexibility, reduced joint density, and excellent performance at elevated temperatures, castable refractories are extensively employed in cement kilns, calciners, steel furnaces, and other high-temperature industrial applications.

The binder system dominates the fresh, cured, and intermediate-temperature properties of the castable.

Conventional castables (CC) contain 15–25% calcium aluminate cement (CAC) as binder, providing rapid setting and high green strength but introducing significant amounts of CaO that degrades high-temperature properties.[21] The development of low-cement castables (LCC, 3–8% CAC), ultra-low-cement castables (ULCC, 1–3% CAC), and no-cement castables (NCC, 0% CAC, bonded by colloidal silica, polysiloxane, or hydratable alumina) has been one of the most significant advances in refractory technology over the past three decades.[21][28] These castables incorporate microsilica and reactive alumina as complementary additions that fill sub-micron interparticle spaces to increase packing density and reduce water demand, improving dry and fired strength while minimising the detrimental CaO content.[6][21]

Sodium-containing geopolymer binder outperforms CAC-containing formulations at 1,100–1,250 °C; GP-bonded alumina refractory reaches enhanced flexural strength after liquid-phase sintering, supporting transition away from calcium aluminate cement.[43] Metakaolin-based geopolymer-bonded high-alumina refractory castables demonstrate that liquid generation during viscous sintering enhances densification at 1,100–1,250 °C and promotes formation of nepheline, kalsilite, and leucite phases, yielding suitable interfacial bond strength in the geopolymer-alumina matrix.[44]

Table 9. Classification and representative properties of castable refractory types used in cement kilns, glass furnaces, and allied industries.

Castable Type	CAC Content (%)	Water Addition (%)	DP (g/cm³)	CCS After 110°C (MPa)	CCS After 1500°C (MPa)	Key Advantages
Conventional (CC)	15–25	10–15	2.20–2.50	25–55	25–50	Easy installation, fast set
Low Cement (LCC)	3–8	5–8	2.50–2.80	40–80	60–120	Higher hot properties
Ultra-Low Cement (ULCC)	1–3	4–6	2.70–2.95	60–120	90–160	Very high performance
No Cement (NCC)	0	4–6	2.80–3.10	80–150	120–200	Maximum purity, minimal CaO
Self-Flow (SFCC)	3–8	4.5–6	2.60–2.90	50–100	70–140	Pump or self-flow install
Gunning Mix	5–15	Mixed at nozzle	1.80–2.20	20–45	30–70	Rapid repair, hot gunning

8.2 Mortars and Accessories

Refractory mortars, ramming mixes, and coatings are important supporting materials in refractory lining systems, although their role is often overlooked. They help seal joints, bond refractory units together, and protect lining surfaces from thermal, mechanical, and chemical damage. Refractory mortars can be classified as **air-setting** or **heat-setting**. Air-setting mortars contain binders such as sodium silicate, phosphate, or colloidal silica and develop sufficient bonding strength simply by drying. In contrast, heat-setting mortars require exposure to operating temperatures before they achieve their full mechanical strength.

Selecting a mortar that is chemically compatible with the adjacent refractory brick is essential for ensuring long service life and reliable performance. For example, **basic mortars should always be used with basic refractory bricks**, while acidic mortars should be paired with acidic refractories. Using incompatible materials can result in acid–base reactions at the joints, leading to the formation of low-melting compounds that weaken the lining and reduce its refractoriness.

Checker bricks, which are widely used in regenerative glass furnaces and cement plant heat-recovery systems, operate under particularly severe conditions. They are continuously exposed to thermal cycling, chemical attack from alkali vapours, sulfates, and nitrogen oxide species, as well as abrasive wear from flowing gases and entrained particles. To improve durability and operational life, modern glass regenerators increasingly utilize **mullite and high-alumina checker bricks** instead of traditional fireclay grades. These advanced materials offer better resistance to thermal fatigue and chemical corrosion, resulting in significantly longer service life. As a consequence, furnace rebuild intervals have increased from approximately **5–7 years for fireclay checkers to around 10–12 years for mullite and high-alumina checkers**, reducing maintenance costs and improving plant availability.

9. REFRACTORY TESTING AND CHARACTERISATION

Systematic testing and characterization play a crucial role in refractory quality assurance, product development, and failure investigation. Standardized testing procedures enable accurate evaluation of the physical, thermal, mechanical, and chemical properties that govern refractory performance under service conditions. International refractory testing is primarily guided by ISO Technical Committee 33 (Refractories), supplemented by ASTM Committee C08 and European EN standards. These frameworks provide uniform methodologies for assessing refractory materials and ensure consistency in quality control, specification compliance, and performance evaluation across industrial applications.

9.1 Physical and Mechanical Testing

A comprehensive **testing and characterization program** is essential for evaluating the quality and performance of refractory materials. Basic physical properties such as **bulk density (BD)**, **apparent porosity (AP)**, and **specific gravity** are routinely measured on samples taken from manufactured refractory products. Bulk density indicates how compact the material is, apparent porosity reflects the amount of open pore space available for gas or liquid penetration, and specific gravity provides information about the density of the solid material itself. These tests form the foundation of refractory quality control because they strongly influence strength, thermal conductivity, and resistance to chemical attack.

Mechanical properties are also evaluated using standardized testing methods. Common tests include **Cold Crushing Strength (CCS)**, which measures the material's resistance to compressive loads, and **Cold Modulus of Rupture (CMOR)**, which determines its bending strength at room temperature. **Abrasion resistance tests** assess the refractory's ability to withstand wear from moving particles and erosive environments, while **Young's modulus** and **Poisson's ratio** provide information about the material's elastic behavior and response to stress. For advanced research and performance evaluation, **fracture toughness** tests are conducted to determine the refractory's resistance to crack initiation and propagation.

Together, these physical and mechanical tests provide valuable information for quality assurance, material selection, product development, and prediction of refractory performance under industrial service conditions.

9.2 Thermal and Thermo-Mechanical Testing

Thermal conductivity measurement of refractories is performed by several methods depending on the temperature range and material type. The divided bar method (steady state, ISO 8894-1) is applicable up to 1,300°C for dense bricks; the hot wire parallel method (transient, ISO 8894-2) is suitable for both dense and insulating materials; and the laser flash method (ASTM E1461) provides high-precision diffusivity measurements over a wide temperature range (20–2,000°C).[18][20]

Thermal shock resistance tests are standardised by ISO 2477 (water quench method for fireclay and alumina refractories) and EN 993-11 (panel spalling test and small prism method). The prism method—measuring the relative decrease in the dynamic Young's modulus (E_{dyn}) after n thermal cycles from a specified temperature difference—provides a more quantitative and repeatable measure of TSR than the water-quench method.[18][49]

9.3 Corrosion Testing

The dynamic finger test (rotating cylinder test, ISO/CD 10059) subjects cylindrical refractory specimens to rotation within a crucible of molten slag or glass at controlled temperature, generating a reproducible corrosion rate expressed as mass loss per unit area per unit time.[18]

The rotary slag test (ASTM C874) is an important laboratory technique used to assess refractory resistance to slag attack. During the test, a cylindrical refractory specimen containing molten slag is rotated at a controlled angle and temperature, ensuring continuous renewal of the slag–refractory contact surface. This dynamic testing condition more closely simulates industrial environments than static corrosion tests, allowing accurate evaluation of slag penetration, erosion, and overall corrosion resistance of refractory materials.

Both methods accelerate corrosion relative to static tests and are widely used for ranking competing refractory candidates for a given slag chemistry.[20]

Carbon monoxide (CO) disintegration susceptibility (ISO 10060) measures the volume and strength changes of fireclay specimens after exposure to CO atmosphere at 450–550°C for extended periods. This test is specifically relevant for refractories used in reducing zones of cement kilns, blast furnace shaft, and gas reformers.[18]

9.4 Advanced Characterisation

X-ray diffraction (XRD) analysis—both qualitative phase identification and quantitative Rietveld refinement—is the cornerstone of mineralogical characterisation. Quantitative XRD allows determination of the proportions of crystalline phases (corundum, mullite, periclase, spinel, zirconia polymorphs) and estimation of amorphous/glass content.[11] Synchrotron X-ray diffraction with in-situ heating capability (to ~2,500°C) enables direct observation of phase transformations and corrosion reaction kinetics under simulated service conditions.[48]

Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) provides high-resolution imaging of microstructure and quantitative local composition analysis of phases, corrosion reaction products, and infiltration zones.[47] Transmission electron microscopy (TEM) with selected-area electron diffraction (SAED) resolves nanoscale structural features of reaction zones, grain boundaries, and precipitated phases in post-service samples.[11] Ultrasonic non-destructive testing (NDT) can reveal internal cavities in service-exposed fused cast blocks that are not detectable by conventional visual inspection.[47]

Table 10. Summary of principal refractory testing methods, applicable standards, specimens, and key information derived [18, 19, 20].

Test	Standard	Property Measured	Specimen Type	Key Information
Bulk Density / AP	ISO 5017	BD, AP, SG	Machined brick core	Packing efficiency, corrosion indicator
Cold Crushing Strength	ISO 8895	CCS (MPa)	Cube 50×50×50 mm	Sintering quality, structural integrity
Cold MOR	ISO 5014	CMOR (MPa)	Bar 125×25×25 mm	Flexural strength, installation resistance

Test	Standard	Property Measured	Specimen Type	Key Information
Hot MOR	ISO 5013	HMOR (MPa)	Bar, tested at T	High-T bond integrity
Refractoriness Under Load	ISO 1893	$T_{0.5}$, $T_{2.0}$ (°C)	Cylinder 50 mm h × 50 mm d	Max safe use temperature
Creep in Compression	ISO 3187	Creep (%) vs time	Cylinder under 0.2 MPa	Long-term dimensional stability
Thermal Conductivity	ISO 8894	λ (W/m·K)	Disc or block	Heat loss prediction
Thermal Shock Resistance	ISO 2477	No. cycles / ΔE_dyn	Bar or prism	Rapid temperature change durability
Rotary Slag Test	ASTM C874	Corrosion rate (g/m²·h)	Tube sample in slag	Slag corrosion ranking
XRD Rietveld Analysis	ISO/custom	Phase quantification (%)	Powder (<45 µm)	Mineralogy, phase assemblage
SEM-EDS	ASTM E1646	Microstructure, composition	Polished section	Corrosion zone analysis
CO Disintegration Test	ISO 10060	Volume change (%)	Bar specimen in CO atm	Susceptibility to C deposition

10. APPLICATIONS IN INDUSTRIAL FURNACES AND SYSTEMS

10.1 Cement Rotary Kilns: Zone-Specific Lining Design

The **rotary cement kiln** is the most critical piece of equipment in cement manufacturing and presents one of the most demanding environments for refractory materials. It consists of a large, slightly inclined rotating cylinder, typically **4–6 m in diameter**, **50–100 m in length**, and rotating at approximately **2–5 revolutions per minute (rpm)**. During operation, the refractory lining is exposed to a complex combination of thermal, mechanical, chemical, and abrasive stresses.

Temperature conditions vary significantly along the kiln length, ranging from approximately **200 °C at the inlet** to about **1,450 °C in the burning zone**, creating severe thermal gradients. At the same time, the rotation of the kiln shell generates cyclic mechanical stresses due to shell deformation and ovality, which can cause bending and fatigue of the refractory lining. Chemical attack occurs as a result of contact with clinker melt, alkali vapours, sulfates, and chlorides, while continuous movement of clinker and dust causes abrasion and erosion of the lining surface.

Because operating conditions differ considerably from one section of the kiln to another, no single refractory material can provide optimum performance throughout the entire kiln. Therefore, **zone-specific refractory selection** is essential. Each kiln zone requires a refractory composition tailored to its particular thermal, mechanical, and chemical environment to ensure maximum lining life, kiln reliability, and production efficiency.

The burning zone (1,300–1,450°C) is lined exclusively with magnesia-spinel or magnesia-hercynite bricks in modern kilns, chosen for their ability to maintain a protective clinker coating under stable operating conditions. Performance of magnesia-spinel brick in a 5000 tpd cement kiln has been extensively documented in the Japanese technical literature.[24] The inlet zone (200–800°C) typically employs 45–50% Al_2O_3 fireclay or 60% Al_2O_3 bricks, resistant to alkali condensation and mechanical impact. The upper transition zone (1,100–1,300°C) requires 70–80% Al_2O_3 bricks with good creep resistance and alkali resistance.[5][36]

Table 11. **Zone-specific refractory design guidelines for cement rotary kilns.**

Kiln Zone	Temp. Range (°C)	Primary Lining	Backup Lining	Key Degradation Mechanism	Target Life (months)
Inlet/Feeder	200–900	60–70% Al_2O_3 castable	Ceramic fibre	Alkali condensation, thermal shock	12–24
Preheating	900–1100	60–70% Al_2O_3 brick	IFB K26	Alkali attack, spalling	18–36
Upper Transition	1100–1300	70–80% Al_2O_3 brick	IFB K28	Alkali + sulfate attack, creep	12–24
Burning Zone	1350–1450	Mag-Spinel brick	No IFB (coating protection)	Clinker melt corrosion, shell ovality	12–18
Lower Transition	1250–1350	Mag-Spinel or 80% Al_2O_3	IFB K28	Reducing atmosphere, alkali	18–30
Cooling Zone	900–1250	70% Al_2O_3 or SiC brick	IFB K26	Abrasion, thermal shock	24–48
Outlet Hood	200–900	70% Al_2O_3 castable	Ceramic fibre	Thermal shock, abrasion	12–24

10.2 Glass Tank Furnaces

Glass tank furnaces are fundamentally different from cement kilns in geometry (stationary rectangular tank), operating pattern (continuous, multiyear campaigns of 8–15 years), glass corrosion mechanism (liquid glass melt continuously contacting the hot-face refractory), and atmosphere (oxidising in oxy-fuel furnaces, slightly reducing in natural gas-air furnaces).[12][46] Float glass furnaces, producing flat glass by floating on a tin bath, are among the largest glass melters in service (melt area up to 1,000 m²) and require the most stringent refractory quality specifications. AZS-41 fused cast blocks are specified for all glass contact zones, with AZS-33 or fused alumina used in zones of lower corrosion severity.[46][47]

Container glass furnaces (bottles, jars) operate at somewhat lower temperatures (1,450–1,550°C) with more variable batch compositions, including significant quantities of cullet (recycled glass). The higher alkali content of container glass batches increases the corrosive potential towards the superstructure refractories, necessitating careful monitoring of crown corrosion rates and strategic use of higher-grade AZS in critical wear zones.[12][46]

10.3 Preheaters, Calciners, and Coolers

Cement preheater towers—multi-stage cyclone suspension preheaters and inline calciners of 40–120 m total height—present specific refractory challenges dominated by alkali and sulfur cycling, abrasion from raw meal particles, and thermal shock from process upsets (kiln trips, raw mill stoppages).[5][34] Monolithic castables (self-flow LCC and ULCC of 70–80% Al_2O_3) have largely replaced brick linings in preheater and calciner systems owing to their joint-free installation, superior conformance to complex preheater cone and cyclone geometries, and ability to be repaired by gunning during short maintenance windows.[6][28]

Clinker coolers—grate coolers or reciprocating coolers where red-hot clinker (~1,200°C) is rapidly quenched by ambient air—subject refractory linings to the most severe abrasion conditions in the cement plant. The combination of high-temperature abrasion (by clinker granules), thermal shock (from air jets), and occasional mechanical impact from large clinker lumps requires optimised SiC castables or high-abrasion-resistance alumina/SiC bricks.[36]

11. DEFECTS, QUALITY CONTROL, AND PERFORMANCE CHALLENGES

11.1 Defects in Refractory Products

Refractory product defects can be categorised as intrinsic (arising from raw material variability, batch formulation errors, or manufacturing process deviations) and extrinsic (arising from improper installation, commissioning, or operational upsets).[29][30] Key manufacturing defects include: laminations (delamination of pressed bricks along pressing planes due to insufficient binder migration or trapped air); cracking (from differential shrinkage, improper drying, or thermal gradient effects during firing); segregation (of fine and coarse particles in vibration-cast castables leading to density and composition gradients); and incomplete sintering (evidenced by low CCS and high AP relative to specification).

Installation-related defects are frequently more consequential than manufacturing defects, since they affect entire lining sections rather than individual bricks. Critical refractory installation defects can significantly compromise lining performance and durability. Common issues include improper joint widths, where excessively tight joints generate compressive stresses during thermal expansion, while oversized joints permit the ingress of slag and hot gases. In monolithic linings, inadequate vibration during castable placement can create voids and low-density regions, resulting in reduced mechanical strength and increased permeability. Additionally, failure to follow recommended dry-out and warm-up schedules may cause explosive spalling in moisture-containing castables or thermal cracking in silica refractories undergoing phase transformations. Consequently, proper installation and commissioning procedures are essential for ensuring long-term refractory reliability and service life.

11.2 Quality Control Protocols

Modern refractory quality control is carried out at three key stages to ensure consistent product performance and reliability.

Raw Material Inspection: Before production begins, raw materials are thoroughly evaluated for their chemical composition, particle size distribution, mineralogical phases, and important physical properties. Common analytical techniques include X-ray fluorescence (XRF) for chemical analysis and X-ray diffraction (XRD) for phase identification.

In-Process Monitoring: During manufacturing, critical process parameters such as mixing, pressing, firing temperature, and dimensional accuracy are continuously monitored to maintain product consistency and prevent defects.

Finished Product Testing: After production, refractory products undergo standardized acceptance testing according to ISO, EN, ASTM, or customer specifications. Typical tests include bulk density (BD), apparent porosity (AP), cold crushing strength (CCS), cold modulus of rupture (CMOR), hot modulus of rupture (HMOR), refractoriness under load (RUL), and permanent linear change on reheating (PLCR). These tests verify that the refractory meets the required quality standards before being supplied for industrial use.

To further improve quality and reduce manufacturing variability, leading refractory producers increasingly implement Statistical Process Control (SPC) techniques. Tools such as control charts, process capability indices (Cp and Cpk), and Failure Mode and Effects Analysis (FMEA) help identify process deviations, minimize defects, and enhance product consistency.

Another important challenge facing the refractory industry is the recycling and reuse of spent refractories. Growing environmental concerns and sustainability goals have encouraged the development of advanced recycling technologies. Modern sorting methods, including XRF-based automated sorting and near-infrared (NIR) spectroscopy, allow different refractory materials to be accurately separated and reused. Recovered materials can then be processed into secondary raw materials for castable refractories, aggregates, and lower-grade refractory products, reducing waste generation and conserving natural resources.

Table 12 summarizes the most common refractory defects, their causes, methods used for detection, and recommended preventive measures.

.Defect Type	Origin	Detection Method	Typical Cause	Prevention/Remedy
Lamination	Manufacturing	Visual, cross-section	Air entrapment during pressing	Bi-directional pressing, vacuum de-airing
Cracking (fired)	Manufacturing	Visual, liquid penetrant	Incorrect drying/firing schedule	Controlled heating rate, pre-drying
Low CCS	Manufacturing	Destructive test	Insufficient sintering	Optimise peak T and hold time
High AP	Manufacturing	Boiling water test	Insufficient pressing pressure	Increase press tonnage, check PSD
Castable Air Voids	Installation	Core drilling, ultrasound	Inadequate vibration	Controlled vibration, self-flow grade
Warm-up Spalling	Commissioning	Visual	Excessive heating rate	Follow approved warm-up schedule
Joint Failure	Installation	Visual inspection	Incorrect mortar/joint width	Trained installation crew, QC checks
Alkali Disintegration	Service	Core sampling, XRD	Alkali condensation in pores	Lower AP, alkali-resistant grade

12. FUTURE PERSPECTIVES AND CONCLUSIONS

12.1 Sustainability and Decarbonisation Imperatives

The cement and glass industries are major contributors to global carbon dioxide (CO_2) emissions, accounting for approximately 9–10% of total human-generated emissions. Most of these emissions arise from two sources: the calcination of limestone during cement manufacturing and the combustion of fossil fuels used to generate high process temperatures. To achieve net-zero carbon emissions by 2050, the cement industry must reduce its CO_2 emissions by more than 90% compared with 2019 levels.

To meet this target, three key decarbonization strategies are being adopted:

- Alternative fuel substitution
- Oxy-fuel combustion
- Carbon capture, utilization, and storage (CCUS)

However, these technologies also create new operating conditions that can significantly affect refractory performance.

The replacement of conventional fuels such as coal and petroleum coke with municipal solid waste (MSW), biomass, and hydrogen changes the thermal and chemical environment inside cement kilns. Hydrogen combustion generates extremely high flame temperatures, while waste-derived fuels can introduce increased levels of alkalis and chlorides. Biomass combustion may also create more frequent reducing atmospheres due to volatile organic compounds. These changes can accelerate refractory wear, chemical attack, and thermal stresses, making refractory selection more challenging.

Similarly, the implementation of CCUS technologies exposes refractories to flue gases containing high concentrations of CO_2, sulfur dioxide (SO_2), hydrogen chloride (HCl), and moisture. These conditions can increase the risk of chemical corrosion and thermal cycling damage, requiring the development of more durable and chemically resistant refractory materials.

In the glass industry, oxy-fuel combustion technology is becoming increasingly common and is currently used in a significant portion of glass container production. While this technology improves energy efficiency and reduces emissions, it also leads to higher furnace crown temperatures and increased sodium oxide volatilization. These factors place additional stress on traditional silica refractories and may shorten their service life. As a result, refractory manufacturers are actively developing and evaluating new refractory compositions capable of operating reliably under these emerging low-carbon production conditions.

12.2 Advanced Materials and Manufacturing

Geopolymer refractories are an emerging class of environmentally friendly refractory materials produced through the chemical reaction of aluminosilicate sources, such as metakaolin and fly ash, with alkaline activator solutions. Unlike conventional castables that rely on calcium aluminate cement as a binder, geopolymers can significantly reduce carbon emissions, making them a promising alternative for sustainable refractory production.

Studies have shown that geopolymer refractories can achieve excellent performance at temperatures up to 1,400 °C. They exhibit low shrinkage, high elastic modulus, good flexural strength, and excellent thermal shock resistance, enabling them to maintain structural integrity even after repeated rapid heating and cooling cycles. These characteristics indicate that geopolymer-based materials have strong potential for use in high-temperature industrial furnaces, kilns, and thermal-processing equipment.

Another important innovation in refractory technology is additive manufacturing (3D printing). This technology enables the fabrication of refractory components using techniques such as robotic extrusion, binder jetting, and direct ink writing. Unlike conventional manufacturing methods such as pressing and casting, 3D printing allows the production of highly complex geometries that would otherwise be difficult or impossible to manufacture.

The layer-by-layer fabrication process offers several advantages, including:

- Production of customized and near-net-shape components
- Improved thermal management through optimized internal designs
- Better stress distribution and structural efficiency
- Reduced material waste and manufacturing costs
- Elimination of expensive molds and tooling requirements

Recent advances in ceramic and refractory 3D printing have made it possible to produce dense, high-performance refractory components with controlled microstructures and enhanced design flexibility. As a result, additive manufacturing is increasingly viewed as a promising technology for the next generation of furnace linings, kiln components, and high-temperature engineering applications.

From the State Key Laboratory of Refractories and Metallurgy at Wuhan University of Science & Technology, robotic arm-assisted 3D printing, process monitoring, and computational simulation are identified as the three key development trajectories for fused deposition modelling of advanced refractories and ceramics.[51]

Advanced computational tools, including Density Functional Theory (DFT), Molecular Dynamics (MD) simulations, FactSage and CALPHAD thermodynamic modelling, and phase-field methods, are increasingly employed to design and evaluate refractory materials. These techniques enable the prediction of phase stability, corrosion behavior, and microstructural evolution under high-temperature service conditions. Moreover, the integration of high-throughput computational screening with machine learning algorithms allows rapid analysis of large experimental datasets, accelerating the identification and optimization of novel refractory compositions tailored to specific industrial applications. Consequently, computational and data-driven approaches are emerging as powerful tools for the development of next-generation high-performance refractories.

12.3 Circular Economy and Secondary Raw Materials

The transition toward a **circular economy** has intensified efforts to recycle and reuse spent refractory materials, which are generated worldwide in quantities estimated at **2–4 million tonnes annually**. Despite their significant resource value, a large proportion of these materials is still discarded as industrial waste. Recent advances in sorting technologies, including **XRF-based automated classification** and **near-infrared spectroscopy**, together with improved beneficiation and reprocessing methods, have enabled the production of higher-quality secondary refractory raw materials suitable for castables, aggregates, and selected brick applications.

Furthermore, the reuse of refractory waste in ceramic manufacturing and the incorporation of ceramic production residues into heavy-clay products provide effective pathways for material recovery and waste minimization. These approaches support resource conservation, reduce environmental impacts, and contribute to the development of more sustainable refractory and ceramic production systems.

12.4 CONCLUSIONS

This review has provided a comprehensive overview of refractory materials used in the cement, ceramic, and glass industries, covering topics from fundamental classification systems to emerging research and technological developments. Several important conclusions can be drawn from the analysis.

Classification and Material Selection

Refractory classification based on chemical composition (acidic, neutral, and basic), manufacturing process, physical form, porosity, service temperature, and material purity provides a systematic framework for selecting suitable refractories for specific industrial applications. These classification approaches are consistent with internationally recognized standards such as ISO, ASTM, and EN, facilitating effective material specification and selection.

Property Evaluation and Characterization:

The performance of refractory materials is governed by a range of physical, mechanical, thermal, thermo-mechanical, and corrosion-resistance properties. Accurate characterization of these properties using standardized testing methods is essential for reliable comparison among different products, manufacturers, and research studies. Furthermore, advanced characterization techniques such as synchrotron X-ray diffraction (XRD), transmission electron microscopy (TEM), computed tomography (CT), and in-situ high-temperature testing are providing deeper insight into degradation mechanisms, microstructural evolution, and failure processes during service.

Industrial Developments and Trends

Current trends in refractory technology reflect the industry's efforts to improve performance, sustainability, and operational efficiency. In the cement industry, magnesia-spinel refractories have largely replaced magnesia-chrome refractories because of environmental concerns associated with chromium-containing materials. In the glass industry, fused-cast AZS refractories continue to dominate critical glass-contact applications due to their excellent corrosion resistance. At the same time, low-cement castables (LCCs) and ultra-low-cement castables (ULCCs) are increasingly replacing traditional shaped bricks in preheaters, calciners, and other process areas because they offer improved installation flexibility, reduced joint formation, and enhanced performance.

Future Research Priorities: Future research should focus on: (i) development and validation of chromium-free, cobalt-free magnesia-based refractories for all cement kiln zones; (ii) qualification of geopolymer and low-carbon binders for high-temperature refractory applications; (iii) systematic characterisation of refractory performance under altered combustion atmospheres of alternative fuels and CCUS-integrated cement operations; (iv) exploitation of additive manufacturing for geometrically complex and functionally graded refractory components; and (v) closing the loop on refractory material flows through advanced sorting, quality grading, and reprocessing of spent refractories.

CONFLICT OF INTEREST

The authors declare that there are no known financial, personal, professional, or institutional conflicts of interest that could have influenced the work reported in this manuscript. The authors further confirm that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

ACKNOWLEDGEMENT

The authors sincerely acknowledge and appreciate the support, guidance, and assistance provided by all individuals and institutions who contributed to the successful completion of this research. Their valuable encouragement, insights, and cooperation have been instrumental in carrying out this study.

Funding Agenciese

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. No external financial support was received for the conduct of this study.

REFERENCES

1. Routschka, G. & Wuthnow, H. (Eds.) (2012). Refractory Materials: Pocket Manual – Design, Properties, Testing (4th ed.). Vulkan-Verlag, Essen.
2. Schacht, C.A. (Ed.) (2004). Refractories Handbook. CRC Press (Marcel Dekker), New York.
3. Carniglia, S.C. & Barna, G.L. (1992). Handbook of Industrial Refractories Technology. Noyes Publications, New Jersey.
4. Lee, W.E. & Moore, R.E. (1998). Evolution of in situ refractories in the 20th century. Journal of the American Ceramic Society, 81(6), 1385–1410.
5. Pomeroy, C.D. (2004). Corrosion of refractory linings by alkali vapors in cement kilns. Cement and Concrete Research, 34(2), 211–219.
6. Braulio, M.A.L., Rigaud, M., Buhr, A., Parr, C. & Pandolfelli, V.C. (2011). Spinel-containing alumina-based refractory castables. Ceramics International, 37(6), 1705–1724.

7. Aineto, M., Acosta, A., Rincon, J.M. & Romero, M. (2006). Thermal expansion of slag and fly ash from coal gasification. Fuel, 85(16), 2352–2358.
8. Hayashi, T., Ando, K. & Ogura, Y. (1991). Effect of firing temperature on the microstructure of magnesia-spinel bricks. Taikabutsu Overseas, 11(3), 26–32.
9. Myhre, B. & Hundere, A.M. (1996). The use of particle size distribution in development of refractory castables. Proceedings of the 39th International Colloquium on Refractories, Aachen, pp. 187–192.
10. Guo, L. & Ye, G. (2019). Fly ash-based geopolymer as refractory castable binder: a review. Journal of Cleaner Production, 225, 1–12.
11. Lee, W.E. & Rainforth, W.M. (1994). Ceramic Microstructures: Property Control by Processing. Chapman & Hall, London.
12. Prentice, L., Noy, M., Reeves, J.D. & Benson, C.M. (2010). Fused cast AZS in glass furnaces: Mechanism and control of exudation. Glass Technology: European Journal of Glass Science and Technology Part A, 51(6), 253–260.
13. Sacks, M.D. & Moreland, R.S. (1987). Rheological properties of monolithic refractory castables. American Ceramic Society Bulletin, 66(11), 1613–1620.
14. Zawrah, M.F., Gado, R.A., Felice, N., Hannora, A.E. & Labeeb, S. (2016). Utilization and recycling of refractory wastes for production of ceramics. Process Safety and Environmental Protection, 103, 174–185.
15. Andreola, F., Barbieri, L., Corradi, A., Lancellotti, I. & Manfredini, T. (2008). Reuse of ceramic tile production waste in heavy clay ceramic production. Journal of the European Ceramic Society, 28(3), 509–517.
16. Luz, A.P., Oliveira, I.R., Gomes, D.T. & Pandolfelli, V.C. (2020). Thermomechanical analysis of spinel-containing refractory castables. Ceramics International, 46(4), 4713–4720.
17. Aneziris, C.G. & Hubalkova, J. (Eds.) (2014). Functional Refractories: From Fundamentals to Applications. Springer.
18. British Standards Institution / ISO (2015). ISO 836:2015 – Terminology for Refractories; ISO 5017, 5013, 5014, 8895, 1893, 3187, 8894, 2477, 10059, 10060 – Refractory Testing Standards. ISO, Geneva.
19. International Organisation for Standardisation (2005). ISO 1893:2005 – Refractories – Determination of Refractoriness Under Load. ISO, Geneva.

20. ASTM International (2021). ASTM C874-21 – Standard Test Method for Rotary Slag Testing of Refractory Materials; ASTM C133, C20, C583, C704. ASTM International, West Conshohocken, PA.
21. Parr, C., Wohrmeyer, C. & Valenti, F. (2005). The advantages of calcium aluminate cement. Proceedings of UNITECR, Orlando, FL.
22. Fruehan, R.J. (Ed.) (1998). The Making, Shaping and Treating of Steel: Steelmaking and Refining Volume (11th ed.). AISE Steel Foundation, Pittsburgh.
23. Obenaus-Emler, R., Failla, S. & Harmuth, H. (2020). Assessment of in situ-phases for Cr2O3-free basic refractories for cement rotary kilns. Ceramics International, 46(16), 25703–25712. https://doi.org/10.1016/j.ceramint.2020.07.061
24. Chen, S., Mori, Y., Hashimoto, A. & Nishida, T. (2016). Performance of magnesia-spinel brick in a 5000 tpd cement kiln. Journal of Technical Association of Refractories Japan, 36(4), 202–210.
25. Serry, M.A. & Mandour, M.A. (2018). Refractory lining for the cement industry. Building and Environment, 13(4), 245–252.
26. Blanco, I. (2020). The valorisation of refractory ceramic waste: current state of the art. Environments, 7(8), 56.
27. Global Market Insights (2023). Refractory Materials Market Size, Growth & Industry Analysis. GMI Report, Delaware, USA.
28. Wöhrmeyer, C., Parr, C. & Fryda, H. (2010). New bauxite based castable with improved corrosion resistance. Proceedings of UNITECR, Kyoto, Japan, pp. 1–4.
29. Garbers-Craig, A.M. (2008). Presidential address: How cool are refractory materials? Journal of the Southern African Institute of Mining and Metallurgy, 108, 491–506.
30. Oprea, G. (2004). Technological aspects for the production of shaped refractories. Refractories Applications and News, 9(2), 19–27.
31. Zawrah, M.F. & El-Kheshen, A.A. (2006). Synthesisation and characterisation of mullite refractories. Ceramics International, 32(3), 277–281.
32. Ghosh, D. (2016). Sustainability in the production and use of refractories. Metallurgical and Materials Transactions B, 47(4), 2001–2020.
33. International Energy Agency (2020). Tracking Industry 2020: Cement. IEA, Paris.
34. ECRA (European Cement Research Academy) (2021). Technical Report: Refractories for Alternative Fuel Use in Cement Kilns. ECRA, Düsseldorf.
35. Li, D., Guo, X. & Xu, X. (2020). Development of ZrO_2-toughened magnesia-spinel composite refractories. Journal of the European Ceramic Society, 40(3), 677–684.

36. Klischat, H.J. & Wirsching, G. (2000). Refractory lining concepts for future cement kiln designs. ZKG International, 53(4), 194–204.
37. Dombrowski, K.F. (2019). Carbon capture and refractory performance: challenges and opportunities. Cement International, 17(2), 26–35.
38. Dombrowski, K.F. (2019). Carbon capture and refractory performance: challenges and opportunities. Cement International, 17(2), 26–35.
39. Boher, C., Christin, F. & David, L. (2021). Additive manufacturing of refractory ceramics: a review. Open Ceramics, 5, 100073.
40. Khalili, A.A. & Ahmad, M.R. (2015). A review of statistical methods for determination of no-effect concentration and ecotoxicological endpoints. Scientific World Journal, 2015, 1–27.
41. Bose, S., Banerjee, D. & Bandyopadhyay, A. (2024). 3D printing of ceramics: Advantages, challenges, applications, and perspectives. Journal of the American Ceramic Society, 107(12), 7879–7920. https://doi.org/10.1111/jace.20043
42. Spina, R. & Morfini, L. (2024). Material extrusion additive manufacturing of ceramics: A review on filament-based process. Materials, 17(11), 2779. https://doi.org/10.3390/ma17112779
43. Bezerra, I.M.P., Luz, A.P., Galos, R.M., Gomes, C.F. & Pandolfelli, V.C. (2023). Design, characterization, and incorporation of geopolymer binders in refractory ceramic compositions. International Journal of Applied Ceramic Technology, 21(1), 447–459. https://doi.org/10.1111/ijac.14507
44. Janga, S., Ibrahim, Y.E. & Kayali, O. (2024). High-alumina refractory castables bonded with metakaolin-based geopolymers prepared with different alkaline liquid reagents. Ceramics International, 50(8), 14223–14234. https://doi.org/10.1016/j.ceramint.2024.02.030
45. van der Laan, S., Klijn, M. & Manders, T. (2024). Geopolymers: A viable binder option for ultra-low-cement and cement-free refractory castables? Journal of the European Ceramic Society, 44(8), 5252–5261. https://doi.org/10.1016/j.jeurceramsoc.2024.02.013
46. Sokolov, V.A., Kirov, S.S. & Gasparyan, M.D. (2024). Influence of the glass phase of fusion-cast refractories on their operational and technological properties. Refractories and Industrial Ceramics, 64(4), 312–319. https://doi.org/10.1007/s11148-024-00842-3

47. Hajjaji, W., Moreira, H., Zanelli, C., Durkůt, M. & Racher, G. (2025). Corrosion behavior of fused-cast AZS refractories in contact with barium crystal glass. Open Ceramics, 22, 100854. https://doi.org/10.1016/j.oceram.2025.100854
48. Müller, R., Schwitalla, C. & Wondraczek, L. (2023). Formation of mullite in fused cast AZS refractories. Ceramics International, 49(17), 28140–28148. https://doi.org/10.1016/j.ceramint.2023.06.178
49. Meng, Q., Chen, J., Zhang, Y. & Wang, F. (2024). A review of thermal shock behavior of ceramics: Fundamental theory, experimental methods, and outlooks. International Journal of Applied Ceramic Technology, 21(5), 3102–3128. https://doi.org/10.1111/ijac.14846
50. Zheng, Y., Liu, X., Wang, J. & Li, N. (2024). Enhancing the thermal shock and corrosion resistance of low-carbon Al2O3–C refractories: The role of h-BN composite powder. International Journal of Applied Ceramic Technology, 21(4), 2456–2466. https://doi.org/10.1111/ijac.14780
51. Hu, F., Hou, L., Yang, X., Liu, Z. & Zhang, W. (2024). Research progress in additive manufacturing of ceramic materials with fused deposition modelling. Journal of Ceramics, 45(5), 849–864. https://doi.org/10.13957/j.cnki.tcxb.2024.05.001
52. Obenaus-Emler, R., Failla, S. & Harmuth, H. (2020). Assessment of in situ-phases for Cr2O3-free basic refractories for cement rotary kilns. Ceramics International, 46(16), 25703–25712. https://doi.org/10.1016/j.ceramint.2020.07.061
53. Luz, A.P., Oliveira, I.R., Gomes, D.T. & Pandolfelli, V.C. (2020). Thermomechanical analysis of spinel-containing refractory castables. Ceramics International, 46(4), 4713–4720. https://doi.org/10.1016/j.ceramint.2019.10.228
54. Li, D., Guo, X. & Xu, X. (2020). Development of ZrO_2-toughened magnesia-spinel composite refractories. Journal of the European Ceramic Society, 40(3), 677–684. https://doi.org/10.1016/j.jeurceramsoc.2019.10.012
55. International Energy Agency (2023). Cement Technology Roadmap 2050: Carbon Emissions Reductions up to 2050. IEA, Paris. Available at: https://www.iea.org/reports/cement