

with SiO₂ contents ≥ 94.5 % represent the largest portion of refractory silica material. Principal applications are in coke ovens (oven sole, heating wall and the upper courses of the regenerator), the superstructure of glass-melting tanks (primarily for soda-lime silicate glass) and hot blast stoves (checker bricks). Lightweight silica bricks (SiO₂ ≥ 91 %, true porosity >45 %) are used primarily for thermal insulation of glass melting tank crowns. Shaped vitreous silica products are mainly used in the glass industry and as a material for hot repairs. Intricate, complex shapes produced using the slip casting process (nozzles, pipes, crucibles, etc.) have a broad range of applications. Unshaped materials (SiO₂ >90 %) include mixes with vitreous silica or quartzite as the raw material basis as well as high quartz silica mortars.

2 Raw Materials

Natural quartzites (for silica bricks) and chemically pure quartz sands (original material for vitreous silica products) are used for the manufacture of silica products. High-quality quartzites have an SiO₂ content of more than 97 %. Differentiation is made in terms of genesis primarily between coarse crystalline uncemented quartzite (predominantly tectonically solidified) and fine crystalline cemented quartzite (solely chemically solidified). Subsequent brick properties are determined in this connection [2]. The transition between these two types is a steady one. Quartzites consist in mineralogical terms of β -quartz (low temperature modification), whereas fired silica bricks mainly contain tridymite and cristobalite. Particular attention must therefore be devoted to the complex polymorphism of SiO₂. This is characterized by a large number of reversible and irreversible modification alterations, associated in some cases with significant changes in volume (Table 1). The total porosity of high-quality quartzites therefore increases on firing from 1 to 2 % to around 14 % (by volume). In addition to firing conditions, the kinetics of quartz conversion are dependent on raw-materials-specific parameters such as the size and distribution of the quartz crystals and the type, quantity and distribution of the mineral impurities always present [3]. The latter are mostly located along the crystal boundaries rather than as crystal inclusions. Due to their high internal surface area and the fine dispersed impurities, cemented quartzites transform more rapidly than the coarse crystalline uncemented quartzites. With crossed polarizers, quartzites formed under high pressure exhibit an undulating extinction of the quartz crystals (lattice faults) under the thin-section microscope. The quartz conversion of such quartzites proceeds better than in the case of

for brick production because severe cracking cannot be avoided even with the most careful temperature control.

more degree of flexibility bricks in 1992.

Table 1
Modification and volume changes of SiO₂

Modification Changes \leftrightarrow reversible \rightarrow irreversible	Transformation Temperature [°C]	Volume Change [%]
$\beta \leftrightarrow \alpha$ -quartz	573	0.8–1.3
α -quartz \rightarrow α -cristobalite	1250 (=1050 *)	17.4
$\beta \leftrightarrow \alpha$ -cristobalite	\approx 260	2–2.8
α -quartz \rightarrow α -tridymite *	\approx 870	14.4
$\gamma \leftrightarrow \beta \leftrightarrow \alpha$ -tridymite *	117–163	0.5
α -tridymite \rightarrow α -cristobalite *	1470	0
α -cristobalite \rightarrow melt	1713 \pm 10	–
α -tridymite \rightarrow melt **	1670 \pm 10	–
fused silica \rightarrow α -cristobalite	above \approx 1150*	\approx 0.9

* in presence of
impurities
** rapid heating

Formation of tridymite only occurs in the presence of impurities at temperatures between approx. 870 °C and 1470 °C. However, cristobalite is nevertheless formed above 1250 °C [4], because the transformation velocity of quartz to cristobalite is much faster than to tridymite. Above around 1470 °C, tridymite is converted to cristobalite which melts at 1713 °C. The chemical analysis, particularly the amounts of fluxes Al₂O₃, TiO₂ and alkalis contained, in particular, is important for assessment and suitability of the quartzites. For refractory use, the combined amount of Al₂O₃ and TiO₂ should be less than 2 % (high-quality grades <0.4 %), while alkalis content should be less than 0.35 % (high-quality grades <0.1 %).

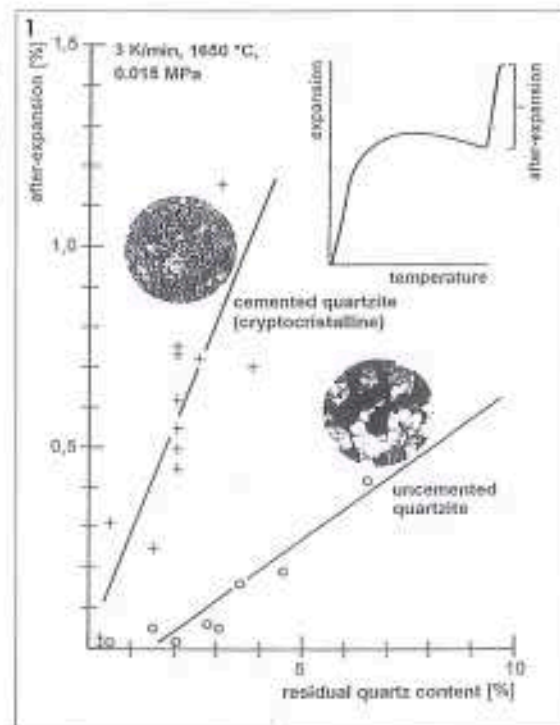
Preferred original material for the commercial production of vitreous silica (density 2.22 g/cm³) are very high-grade quartz sands with SiO₂ of more than 99.5 % which are electrically melted at around 1800 to 2100 °C (by means of carbon electrodes or electric arc) and then rapidly quenched (bar melting process and rotary melting process [5]). The glassy solidified turbid raw material is also referred to as fused silica (bulk density 2.00 to 2.10 g/cm³), exclusively closed porosity is around 5 to 7.5 % with a pore size of up to 0.5 mm; impurities content is less than 0.5 %. Translucent silica glass, also referred to as vitreous silica, is denser (bulk density approx. 2.21 g/cm³) and contains only traces of impurities [6]. Characteristic properties of vitreous silica as a refractory material are its extremely low coefficient of thermal expansion ($\alpha_{30-1600}$ °C approx.

[7] and also has a positive effect on brick strength. Grain size guidelines generally applicable in coarse ceramics for achievement of a dense structure are applicable only to a limited extent in the production of silica bricks. The reason for this can be found in the influence of grain size distribution acting in superimposition on conversion behaviour during brick firing ("firing growth"). The prepared mix is moulded on hydraulic presses (forming pressure 80 to 100 MPa) or, in the case of extremely complicated shapes and small quantities per unit, manually using air-ramming method. The non-dried blank is extremely sensitive and must therefore be handled carefully. After complicated firing at around 1420 to 1480 °C and a shape-dependent total firing time of 1 to 3 weeks, silica bricks have grown linearly by approx. 4 to 5 % as a result of the conversion of quartz to tridymite and cristobalite (densities of low-temperature modifications in g/cm³: β-quartz 2.65, β-cristobalite 2.32, γ-tridymite 2.27). The degree of conversion is dependent not only on firing parameters and batch composition, but also on brick shape [8]. Increasing firing time and mineralizers promote the formation of tridymite. Other phase constituents of silica bricks are pseudo-wollastonite (β-CaO·SiO₂, <5 %) and an amorphous SiO₂-CaO-

is reached at 800 to 1000 °C. Towards higher temperatures, the bricks exhibit reversible negative expansion (normally 0.1 to 0.2 %) which is attributable to the lattice contraction of tridymite. Due to the slight change in thermal expansion, silica bricks have excellent resistance to cyclical temperature changes above 600 °C. Appropriate care is required at lower temperatures, in order to avoid cracking. Silica bricks have an extraordinary good hot stability under compression in high-temperature ranges, since the melt phase content dependent on flux content only declines noticeably above 1600 °C [12]. In extremely low-flux brands for glass-tank furnaces, the sum of Al₂O₃ content and double the alkali content is ≤0.5 % [13–14]. One possibility for the manufacture of very dense silica coke-oven bricks is the use of fine-grained Si₃N₄ or SiC as a part of the batch composition (0.5 to 10 %). Cristobalite forms by oxidation during brick firing above approx. 1200 °C and it fills the intergranular pores. However, a further conversion may occur during service in case of insufficient oxidation and can cause destruction of the bricks.

Silica glass-furnace bricks are used at temperatures between approx. 1300 and 1650 °C. Thermal and corrosive stresses in coke ovens are significantly lower (mean heating-flue temperatures between 1200 °C and 1400 °C). During operation in a temperature gradient, silica bricks develop zones with different microstructures which, in some cases, are implied by the migration of intrinsic and infiltrated foreign constituents [15–16]. In the hot brick zones, the different SiO₂ modifications uniformly transform to cristobalite above approx. 1450 °C and in a temperature range between 1300 and 1400 °C into tridymite. This "trans-crystallization with crystal growth" proceed without any change in volume (differing degree of order between primary and secondary formation). These processes result in a significant improvement in thermo-mechanical property features in the hot-side zone of the bricks [11, 17–18]. For example, an increase of around 15 % in thermal conductivity at 1200 °C has been measured in used silica coke-oven bricks, with beneficial effects for the coke-oven's heat balance [11]. The cristobalite zone formed in glass-furnace bricks shows a substantial increase in thermal conductivity (factor 2, referred to the new brick), resulting in positive effects for corrosion behaviour (dissipation of corrosive high-Na₂O melt into colder brick zones) [15]. Silica bricks are readily attacked by basic slags and iron oxide at high temperatures in a reducing atmosphere. The corrosion behaviour against acid slags is good.

Fig. 1
After-expansion of
various silica bricks
with a different raw-
material basis
depending on
residual quartz
content [%]



amorphous-phase is slightly greater than in dense silica bricks. Bulk density varies between around 0.6 and 1.25 g/cm³ and, corresponding to this, cold crushing strength between 1 and 6 MPa. Maximum thermal expansion is 1.2 to 1.3 %. Thermal conductivity at 1000 °C exhibits figures of 0.5 to 0.85 W/m-K, depending on brick bulk density. Maximum service temperature is between 1500 and 1650 °C. Lightweight silica bricks are used largely for the insulation of silica brick constructions, especially the crowns of glass-tanks (lining variant, Fig. 2). Appropriate thermal insulation also has a positive effect on the wear behaviour of the silica crown [19].

5 Shaped Fused Silica Products

Outstanding refractory properties are the extremely low thermal expansion and excellent thermal shock resistance in the temperature range up to approx. 1100 °C. Vitreous silica also has excellent corrosion resistance in acidic media. Another reason for its use in glass melting furnaces is the benign dissolution behaviour in contact with the glass melt (characteristic of all SiO₂ products).

Compact fused cast shapes or bricks with lengths up to 2 m are produced from the electrically melted raw blocks by cutting and grinding or milling using diamond tools. A dense structure without open pores is characteristic (bulk density up to 97 % of theoretical density). Large shapes are used in glass contact areas of glass-tank furnaces for the melting of low-alkali or alkali-free high-SiO₂ glasses (e.g. borosilicate glasses) at temperatures above 1470 °C. During service, vitreous silica then re-crystallises entirely to cristobalite, whereas the volume stability is retained up to 1700 °C (refractoriness under load, t₀ value approx. 1700 °C). If heating-up under load occurs too quickly, softening can take place at approx. 1350 °C as a result of inadequate cristobalite formation (t₀ value 1400 °C). Compared to fused cast AZS materials, fused cast silica has a more stable electrical conductivity during service, a fact from which a better corrosion behaviour in electrically heated tanks can be derived [6]. Once devitrified to cristobalite, the advantageous properties of vitreous silica products are lost.

In the case of ceramic manufacture, the granular fused silica mixes containing special binders are shaped by uniaxial as well as isostatic pressing, and by slip-casting. In the latter case, a slip with approx. 90 % solids content and defined rheological properties (use

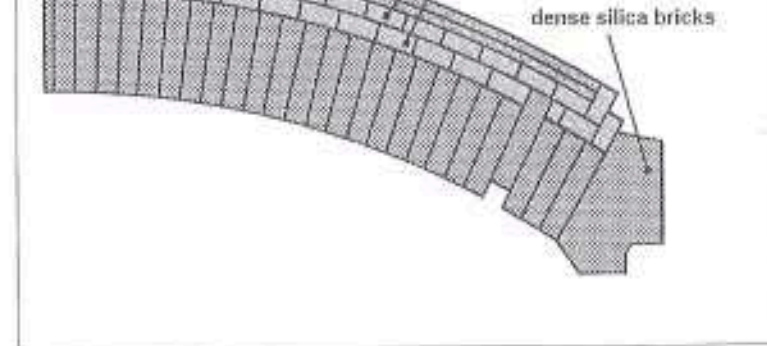


Fig. 2
Crown insulation,
2-layered brick firing
with special silica
insulating bricks

of deflocculants) is cast into porous plaster moulds. Shape-dependent settling time varies between several hours and one week. Particular importance attaches to mould-making in terms of anticipated body formation. The dried castings have a high green strength, permitting finishing to ultimate dimensions by cutting and drilling. Strength is increased by firing at temperatures below 1100 °C (linear firing shrinkage 0.05 %). More complicated shapes are used, for example, in the steel industry (pipes, submerged entry nozzles and slag protection rings for continuous casting), the glass industry (funnels and rings for container glass, pushers and rollers for flat glass) and in furnace engineering (rollers and slabs) [20].

Ceramic shaping of bricks is normally accomplished by uniaxial pressing (mechanical and manual) or by vibration-casting. Additives containing P₂O₅ or CaO are used as chemical or hydraulic binders (content in formulation approx. 1 to 7.5 %). If necessary, the blanks are tempered at temperatures between 150 °C and 1000 °C in order to enhance strength, resp. to volatilise hydration water. Such shaped fused silica bricks are used particularly in coke-oven maintenance as hot-repair material for the chamber walls [21–23] and also, for example, as curtain wall bricks in the batch feed zone of glass melting furnaces. Pressed fused silica bricks for use in coke ovens have a CaO content of 2.5 to 4 % (Al₂O₃ 0.3 to 0.6 %) and contain around 15 % β-quartz. Tridymite and cristobalite are formed during operation, mineralogical composition then becoming equivalent to those of dense silica bricks. Properties of vitreous silica products are listed in Table 3.

6 Unshaped Silica Products

Quartzite castables with added sintering agents (e.g. frits) or hydraulic-activated bonding agents have an

boric acid anhydride (B_2O_3) (dry running mix). Such mixes are used, for example, in induction furnaces for melting of steel or copper. Vitreous silica is also a raw-material basis for hot-repair castables (generally with a grain size < 6 mm).

The utilisation of a hydraulic bond (CaO-containing) or a chemical bond (containing P_2O_5 or sodium silicate) ensures appropriate development of strength during service (primarily in the glass industry, SiO_2 content 90 to 98 %). A fused silica-based gel-bond castable is recommended for hot repairs on coke ovens (sidewalls, roof and floor) and glass melting tanks (crown and doghouse) [24]. Consistency is adjusted via the quantity of silica gel added (mixing liquid); SiO_2 content is around 99 %.

Fine-grained mortars (grain size < 0.6 mm) are mixtures of quartz sand, silica flour, and clay (air-setting mortars, possibly with the addition of organic plasticizers). They are used for laying and jointing of silica bricks. The content of banding clay (2 to 15 %) is selected according to the particular application. Mortars for use in glass tank superstructures in zones of high thermal and corrosive stress have a significantly lower bonding clay and flux content (SiO_2 content 99 %) than the coke-oven mortars.

Natural loamy clays also belong to the latter, if these meet the standardised requirement criteria [25]. Silica mortars are also used for installation of semi-silica bricks ($\text{SiO}_2 \geq 65$ %) in coke-oven construction, a few percent by weight of cement generally being added to the mortar for use in the lower temperature range < 900 °C (regenerator). An alternative achieved via the addition of borax (2 to 5 %) is also suggested [26].

The behaviour on application of these mortars is extremely complex due to numerous influencing parameters (e.g. raw-materials composition, conversion behaviour under thermal and corrosive stresses) [15, 27].

Instruction for preparation and installation guidelines for castables, mixes and mortars can be obtained from the manufacturer.

References

[1] European Standard EN 12475-1 [1998]: Classification of Dense-Shaped Refractory Products – Part 1: Alumina-silica products. Brussels [8], European Committee for Standardization, 1998

[10] K.E. Lepère, E. Overkott, et al.: Requirements with Respect to Silica Bricks as Building Material for the Next Coke Oven Generation. *Cokemaking International* 1 [1992] 28–32

[11] F. Brunk: Silica Bricks for Modern Coke Oven Batteries. *Cokemaking International* [2000] 37–40

[12] P.N. Mohanty, P.N. Singh, G.D. Singh: Silica – A Critical Study, Part 2. *Refractories Journal* (1982) [3] 10–17

[13] American Standard ASTM C 416 (1998): Standard Classification of Silica Refractory Brick. West Conshohocken, PA [USA]: American Society for Testing and Materials, 1998

[14] China Standards on Refractories. *China's Refractories* 8 [1999] [4] 34–38

[15] F. Brunk, W. Weßling: Verhalten von Silika-Gewölbesteinen in Glaswannen. In: XXXVI. Internat. Feuerfest-Kolloquium on Refractories in Glass Industry (1993) [20] 23–26

[16] J.D. Panda, G. Goswami: Mineralogical Investigation of Used Indian Silica Coke Oven Bricks. *Iron and Steel Review* 39 [1996] [8] 26–28

[17] Y. Suenga, H. Tabuchi, H. Uemura: On Silica Brick for Glass Tank Crown. Shinagawa Techn. Report (1980) [24] 1–6

[18] A. Wereszczak, H. Wang, et al.: Postmodern Analyses of Salvaged Conventional Silica Bricks from Glass Production Furnaces. *Glastechn. Ber. / Glass Sci. Technol.* 73 [2000] [6] 165–174

[19] J. LeBlanc: Impact of Silica Refractory Attack on Soda Lime Oxy-Fuel Furnaces. *L'industrie Céramique & Verrière* [1999] [945/2] 118–123

[20] P. Schulz: Schlickergießen von amorpher Kieselsäure von großformatigen und komplizierten Teilen. *Keram. Z.* 38 (1986) [8] 442–445

[21] J. Pairier, J.M. Leroy, et al.: Non-Dilating Silica Elements for the Repair of Coke Ovens: Results and Prospects. *La Revue de Métallurgie* 96 [1999] 709–713

[22] F. Brunk, J. Spitz: Experience with Coke Oven Wall Repairs Using Low Thermal Expansion Silica Brick Material. *Cokemaking International* 10 [1998] 74–76

[23] E.W. Itell, C.T. Henson: Coke-Oven Wall Repairs Using Low Thermal Expansion Fused Silica Brick. *Iron and Steel Engineer* [1991] 50–53

[24] S. Banerjee: Versatility of Gel-Bond Castable/Pumpable Refractories. *Refractories Applications* [2001] [1] 3–5

[25] German Standard DIN 1089-3 (1990): Refractories for Use in Coke Ovens. Part 3: Mortar for Silica and Fireclay Bricks, Requirements and Testing. Berlin, DIN Deutsches Institut für Normung e.V., 1990

[26] M.I. Prokopenko, et al.: Mortar for Lining Coke Batteries by Zones. *Refractories* 34 [1993] [7/8] 443–446

[27] H.J. Koschlig, W. Sieweke: Silica Mortar for Coke Ovens – Effects in Brickwork, Composition and Properties. In: UNITECR '91 Congress Proceedings. The German Refractories Association [1992] 453–456