Dense Silica – Properties, Production and Perspectives

M. Kotouček, P. Kovář, K. Lang, L. Vašica, L. Nevřivová

The paper introduces a new type of silica bricks, describes the technology of production and achieved properties of silica material. Significant density of green brick, which is an important condition for achievement of low porosity of burnt product, can be achieved by using of appropriate composition of raw materials and appropriate plastification additives.
Rate of material density is one of the determining factors affecting resistance of silica material. Dense materials are more resistant to the diffusion of aggressive atmosphere elements in furnaces and have increased thermal conductivity and abrasion resistence which are characteristics of the material required especially by the coke industry.

1 Introduction

Silica is undoubtedly one of the traditional refractory materials used for many years in a number of industrial areas. Even though several new materials with better characteristics than silica have been developed recently it still has got due to its specific properties irreplaceable position in many applications.
P-D Refractories CZ a.s. performs continuous development of silica materials. This development is based on use of high quality raw materials and is focused on a search for suitable additives having impact on rheology of working mass, physical and chemical parameters and thermal properties of the produced silica material.
Silica bricks are often exposed to an extreme thermal wear under operation conditions. They are also mechanically stressed and exposed to effects of aggressive agents. That is why silica bricks must excel mainly in characteristics of refractoriness under load, chemical purity, resistance to alkali vapours etc.

2 Application areas

The main application areas for silica materials traditionally are in linings of glass furnaces, coke oven batteries and hot blast stoves.
Glass producers tend to increase output and intensify the melting process which brings high demands on quality of refractory linings, especially of crowns. These linings are exposed mainly to alkali vapours. Their impact causes the disruption of lining due to the condensation of aggressive components of furnace atmosphere within the crown material (Fig. 1). This corrosion is especially intensive when oxygen combustion is used and the temperature below the crown reaches up to 1680 °C.
Silica bricks form a major part of coke oven battery lining. This is determined by the fact that they have high chemical resistance and desired thermal and mechanical characteristics for use within the critical parts of the battery. Silica brickwork in the heating walls

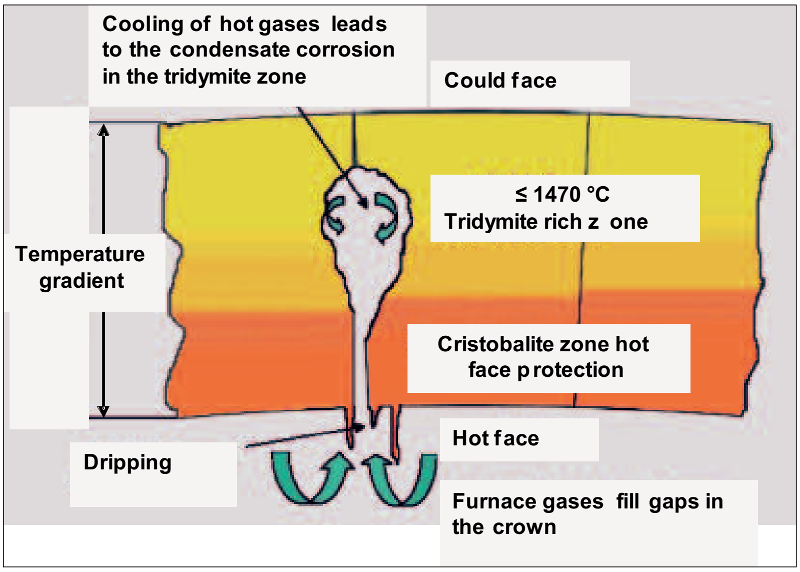

Fig. 1 Principle of glass furnace crown lining deterioration under attack by waste gases

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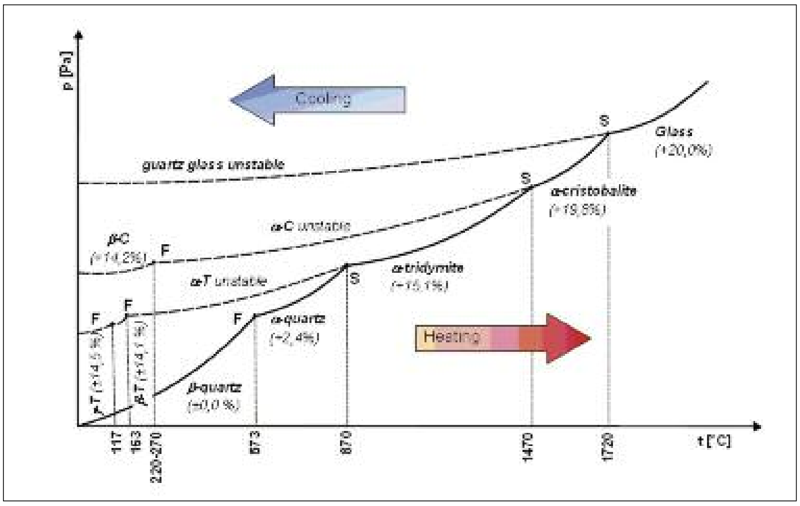

Fig. 2 The temperature dependence of the quartz transformation changes scheme

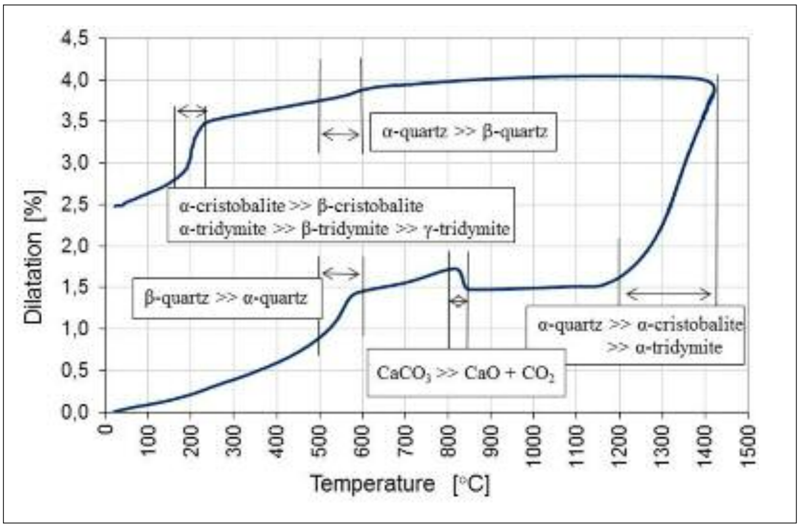

Fig. 3 Record of linear changes of silica material during firing (illustrative example only, showing not finished quartz transformation, see slight curve decrease at 600 °C during the cooling phase)

is exposed to a combination of pressures and temperatures, which may reach 1450 °C. Current trend is to enlarge dimensions of chambers and decrease thickness of the heat-exchanging parts of heating walls. These modifications – led by efforts to intensify the heat transfer through walls into the coal and to increase the production capacity of facilities –define new quality requirements of materials used in heating walls.

3 Motivation of development and production of dense silica

The above mentioned implies that customers require silica material which not only withstands very high temperatures and aggressive atmosphere (glass industry) but also performs high quality combination of thermal, technical and mechanical characteristics (coke industry). One of the possible ways of combining these requirements is production of silica bricks with a structure of higher density and high chemical purity.

4 Principles of silica bricks production

Basic raw material for silica bricks production is chemically pure quartzite with a volume of SiO_2 above 99 %. We recognize two basic types of quartzite based on the character and results of the rock-forming process. These are so called fine-crystalline and coarse-crystalline quartzite. The quartzite types have a decisive impact on the transformation behaviour of the material during firing which is always complicated. Besides quartzite, quartz sands of a similar chemical composition are used for silica bricks production.

Working mass is prepared from the defined grain sizes of crushed quartzite and quartz sands. The mass is enriched with hydrated lime $Ca(OH)_2$ (up to 4 %) which serves as a binder and as an accelerator of the quartz transformation (mineralizing agent). Finding the most appropriate quantity of this agent is very important for achieving the desired mechanical strength of the product without any substantial decrease in its thermal and mechanical properties. Iron oxides mainly in form of iron dust are also used as a mineralizing agent. Together with the temperature conditions the iron oxides content determines the mineralogical composition of the produced silica material.

Forming of the raw material mixture into shapes is performed using hydraulic press machines. Firing goes on in tunnel or shuttle kiln with a precise regulation of temperature and firing speed which prevents occurrence of cracks within the products.

Quartz is transformed to cristobalite and tridymite during the firing of silica materials (Fig. 2). These changes are always connected with a considerable volume expansion, approx. by 12 – 15 %. Total firing time ranges between 150 – 250 h; maximal temperature is 1430 °C.

There is a visible decline on dilatation curve during a cooling phase under 300 °C. This is caused by the displacement changes of the formed cristobalite and tridymite (Fig. 3). While the fired silica can be cooled down quite quickly up to 300 °C, below this temperature the cooling speed must be slowed down to only 5 K/h. Faster cooling could result in tension causing cracks within the material.

5 Application of new approaches

Silica bricks with bulk density higher than 1880 $kg \cdot m^{-3}$ and porosity lower than 18,5 % can not be easily produced by the technology described above. That is why new and better production procedures are searched for and tested. Also new raw materials were searched for in order to get better compaction. Grain size curve of the working mass needed to be optimized too as because one of the conditions for getting low porosity of the fired material is low porosity of the products before firing. For example granulometry composition of the raw material mixture in the sub-micron area is affected by use of the finest quartzite with particles of 0,1 – 0,2 µm.

6 The real production process test results

The results of performed R&D activities were used for real production process of silica bricks with high density and apparent porosity of 13 %. In Tab. 1 are the achieved values compared with values of silica bricks having higher porosity (17 % and 21 %).

Compact structure of new silica material corresponds with the achieved figures of bulk density respectively with apparent porosity of 13 %. Appropriate adjustment of firing regime leads to a perfect quartz transformation by all kinds of silica material.

7 Technical, thermal and mechanical properties

Testing of thermal and mechanical properties forms an integral part of assessment of refractory materials and judgment of their behaviour in real operation conditions. Traditional representative of such properties is refractoriness under load. Characteristics of creep have also become a standardly checked property. Figures of both characteristics of the compared silica materials are indicated in the Tab. 2.

It is known that behaviour of silica in heat is negatively influenced by all the accompanying compounds of SiO_2 within the material. The major role is played by contents of Al_2O_3, Na_2O and K_2O. Comparison of refractoriness under load figures indicated in Tab. 2 and contents of the mentioned oxides indicated in Tab. 1 shows that the differences in values of refractoriness under load more or less correspond with the differences in chemical composition. Difference in refractoriness under load between high density silica and standard silica with 21 % porosity may seem to be not that big. However, especially in case of glass melting aggregates with oxygen fuel technology where the operation temperatures reach almost melting temperature of pure SiO_2, every extra grade of refractoriness under load is very important.

As far as creep is concerned, its dependence on chemical composition of silica material and its compactness is not that obvious. The

Tab. 1 **The basic characteristics by different porosity of silica bricks values of the compared silica bricks types**

Characteristics \ Silica		AP 13%	AP 17%	AP 21%
Bulk density	[kg·m^{-3}]	1990	1920	1825
Apparent porosity	[%]	12,7	16,6	20,8
Apparent density	[kg·m^{-3}]	2280	2300	2305
CCS	[MPa]	113,0	66,0	48,0
Chemical composition:				
SiO_2	[%]	97,50	96,40	96,20
Al_2O_3	[%]	0,30	0,32	0,45
TiO_2	[%]	0,03	0,03	0,02
Fe_2O_3	[%]	0,45	0,50	0,46
CaO	[%]	1,50	2,30	2,50
$Na_2O + K_2O$	[%]	0,14	0,17	0,21
Phase composition:				
Cristobalite	[%]	43	43	39
Tridymite	[%]	37	47	41
Residual quartz	[%]	< 0,5	< 0,5	< 0,5

Tab. 2 **Refractoriness under load as per EN ISO 1893 and creep characteristics of silica materials as per standard DIN 1089-1; *Creep at 1500 °C/0,2 MPa between 5th and 25th h of measurement**

Characteristics \ Silica		AP 13%	AP 17%	AP 21%
RUL:				
$T_{0,5}$	[°C]	1677	1673	1669
$T_{1,0}$	[°C]	1679	1678	1675
CREEP:				
Z_{5-25} *	[%]	0,055	0,045	0,053

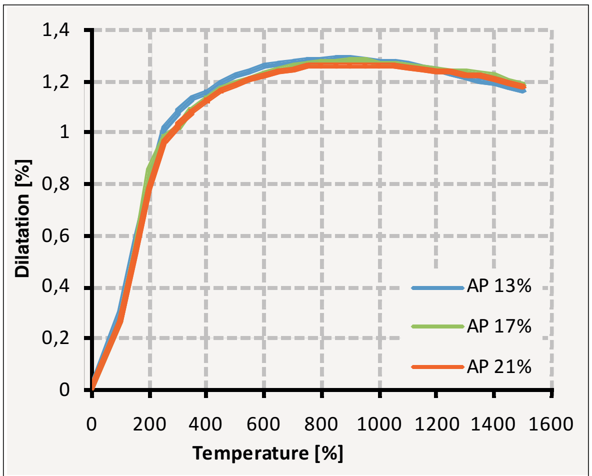

Fig. 4 **Typical curves of thermal dilatation of silica material with various porosity values**

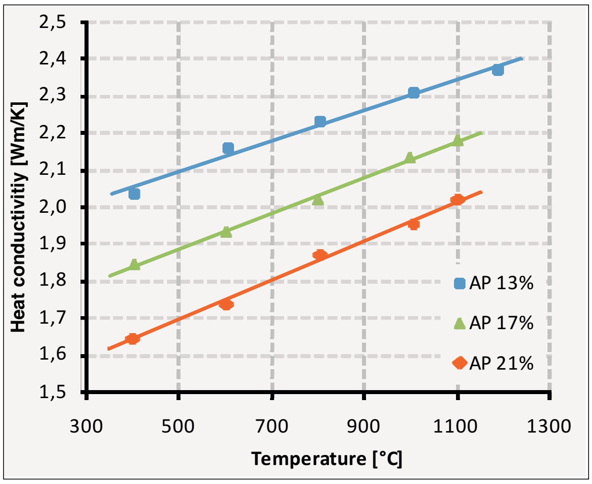

Fig. 5 **Test results of thermal conductivity of silica materials as per ČSN EN 993-15 (heating wire method)**

Fig. 6 **Silica sample with apparent porosity of 21 % after the abrasion resistance test, volume of removed material V = 5,8 cm³**

Fig. 7 **Silica sample with AP = 13 % after the abrasion resistance test, volume of removed material V = 2,8 cm³**

explanation is found in technical possibilities of the accessible measurement devices and its sensitivity of scanning linear changes of the tested samples. Another reason is in the heterogeneity of silica material composition, the effects of which may be more important than effects of chemical composition, tension and temperature.

When discussing about the behaviour of silica material products in heat, it should be mentioned that differences in porosity and chemical composition are not substantially reflected in thermal expansion of silica material. Fig. 4 shows that dilatation curves of the compared silica materials are almost identical.

An important physical constant of refractory materials, playing substantial role e.g. for silica bricks for coke oven battery heating walls, is coefficient of thermal conductivity. Thermal conductivity of silica materials (material with heterogenic systems including besides solid phase also pores) depends mainly on porosity. As the newly developed silica material has much lower porosity we assessed new thermal conductivity tests at *Technical University Ostrava.* The results are presented in Fig. 5. The measurements confirmed the expected increase in thermal conductivity of the highly compacted silica material. This property presents an important element for intensification of coke production or for decrease of its energetic demands.

The abrasion resistance should be also mentioned when discussing about the high mechanical strength of the new silica material. Tests of abrasion resistance as per ČSN EN ISO 16282 were carried out in order to discover the relation between density and abrasion resistance. This relation is extremely important especially for bottoms of coking chambers. The enormous impact of density level on wear of material due to abrasion is presented in Fig. 6 and Fig. 7.

8 Conclusion

Silica products are irreplaceable for industrial facilities in glass and metallurgy sector (glass furnaces, coke oven batteries, hot blast stoves). In all these aggregates silica bricks are exposed to intensive thermal, mechanical and corrosive wear. High and stable quality of the used materials for linings is required for reliable and long-term operation of these aggregates.

P-D Refractories CZ a.s. therefore continuously improves the quality parameters of its products. This happens even on top of the internationally recognized quality standards. As far as development of silica materials is concerned we work permanently on increasing the density values and improving the thermal and mechanical properties of the products used in extreme operation conditions which are dominantly present at bottoms and in heating walls of coke oven batteries and in crowns of glass melting facilities. Aim of this paper was to provide information about one of the results of this development process.

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