

The Influence of Mineraliser Granulometry on Dense Silica Brick Microstructure

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Abstract—This entry concerned with dense silica bricks microstructure was produced as a part of a project within the Technology Agency of the Czech Republic which is being implemented in cooperation of the biggest producer of refractories the P-D Refractories CZ company with the research organisation Brno University of Technology. The paper is focused on the influence of mixture homogenisation and the influence of grain size of the mineraliser on the resulting utility properties of the material as well as its microstructure. It has a decisive influence on the durability of the material in a building structure. This paper is a continuation of a previously published study dealing with the suitability of various types of mineralising agents in terms of density, strength and mineral composition of silica brick.

The entry describes the influence of the method of mixture homogenisation and the influence of granulometry of the applied Fe-mineralising agent on the resulting silica microstructure. Porosity, density, phase composition and microstructure of the experimentally prepared silica bricks samples were examined and the results were discussed in context with the technology of homogenisation and firing temperature used. The properties of silica bricks samples were compared to the sample without any Fe-mineraliser.

Keywords—Silica bricks, Fe-mineraliser, mineralogical composition, new developed silica bricks.

I. GENERAL INTRODUCTION

SILICA brick is a refractory which is significant from the chemical point of view by its high content of SiO_2 (more than 93 %). As a mineral, it is composed of various modifications of SiO_2 , particularly β -cristobalite and γ -tridymite [1]. Furthermore, it is composed of a low amount of unmodified β -quartz, calcium orthosilicates, and vitreous phase [2].

The usage of refractory materials, usage of silica bricks as well, is influenced by technological development in the industries where these materials are applied. Their constantly increasing technical quality is an accompanying effect referred to as “Hara-kiri effect.” Despite the unavoidable trend of continuous stagnation of the volumes required by industries, new refractory products are being developed, new technologies invented or new raw materials utilized. One of

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such products is silica material which is still used for its specific properties.

The use of silica material is quite specific, being implemented mainly in the following 3 areas with completely different utilization (Fig. 1). The biggest volumes are utilized in the construction of coke oven batteries, silica is still hardly replaceable in the crowns of glass melting furnaces and it is being used ever more frequently and also for the top parts of hot blast stoves in metallurgy. Even though the application of silica materials in these 3 areas is very effective there is still a potential for reaching an even higher level of quality. The success of this material based on SiO_2 is determined mainly by its outstanding performance at high temperatures. The melting point of SiO_2 is the lowest one in the category of technical oxides (1726°C) which is why firing is the critical part of the manufacturing process.



Fig. 1 Application of silica in coke production, glass industry and metallurgy

Despite this fact it is clear that the desired changes of parameters cannot be attained only by making changes in the firing regime. It is essential to attain maximum density at raw conditions and optimal dosage of mineralisers (maintaining thermodynamic properties) in order to have the optimal solution.

Among other issues related to the use of silica bricks are adapting the material's behaviour to various operational conditions and optimizing its properties for the requirements of specific applications.

Reaching better chemical (higher SiO_2 content and lower content of melting oxides), physical (lower apparent porosity and higher CCS) and thermodynamic properties (lower speed of creep) is mostly linked with higher thermal conductivity which is not always an advantage especially in glass industry application.

A partial problem is also posed by the specification of “Alkali-resistance test (as per OWENS-ILLINOIS)” where corrosion resistance test at 1370°C is required. This temperature will not always correspond with operation temperatures which are mostly higher. There will be a

difference in the obtained values of penetration and melt-off. Also result interpretation of so few tests may be problematic.

An entirely different situation can be seen in case of application in coke-making industry (Fig. 1) where greater thermal conductivity is desired and coking temperatures are much lower than corrosion test temperature. An improvement of the monitored parameters is provable and there are no problems with result interpretation.

As the text above reveals, the different behaviours of individual applications must be taken into account when optimising the properties of silica materials.

II. OBJECTIVE

During the production of silica materials it is advisable to use such additives which accelerate the formation of melt during silica bricks firing and have an influence on its resulting mineralogical composition. Such additives are e.g. Fe-pigments and Fe-dust.

The goal of this research was the investigation of the influence of the granulometry of these Fe-mineralisers on the properties of silica bricks which have the greatest impact on its durability in the structure of an oven (strength, porosity, bulk density and mineralogical composition). Simultaneously, the influence of the method of homogenising and the length of firing on these properties was observed.

III. MATERIAL

A. Basic Raw Materials

The main raw material for silica bricks production is quartzite which serves as the main source of SiO₂. Other raw materials are quartz sand, silica scrap and auxiliary materials such as lime, sulphite lye, plastifying and mineralising agents, Fig. 2.

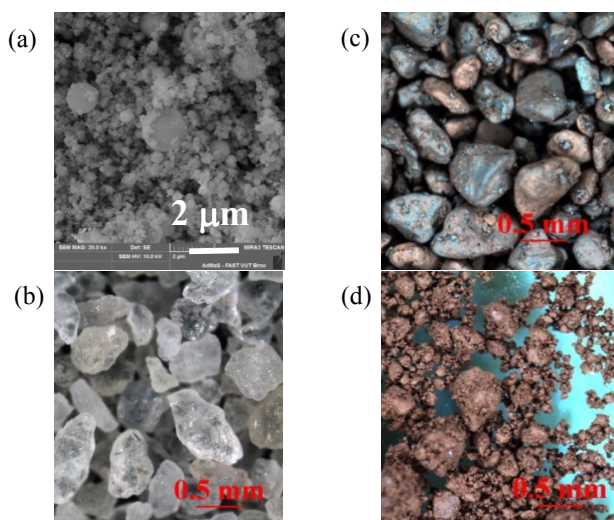


Fig. 2 Grain shape of the raw materials used, (a) microsilica, (b) quartz sand, (c) mineraliser D, (d) mineraliser B

The following components were used in making the specimens; quartzite of grain size 0-1mm, 1-2mm, 2-3mm,

quartz sand of grain size 0-1mm, silica flour with grain size under 0,09mm, microsilica MS 983 from the Elkem company and two types of Fe-mineralisers of varied granulometry.

Mineraliser B – grain size below 200 µm

Mineraliser C – grain size below 50 µm

Mineraliser D – grain size below 1000 µm

B. Specimen Preparation and Identification

The experiment used a basic formula for the production of dense silica bricks, identified by the letter A (no mineraliser), which was modified by the above-specified mineralisers.

TABLE I
 LIST AND IDENTIFICATION OF USED FORMULAE

Formula	Fe-mineraliser	Method of mineraliser homogenisation in the mixture
A	none	24 hours in dried state
B	Particle size under 200µm	24 hours in dried state
C1	Particle size under 50µm	24 hours in dried state
C2	Particle size under 50µm	3 minutes in wet state
D	Particle size under 1000µm	24 hours in dried state

After mixture homogenisation with moisture content ranging from 4–5%, cylindrical specimens with the diameter 40mm were pressed. The pressing was performed at 20kN. After drying, (Fig. 3) the specimens were fired in a laboratory furnace at the temperature 1415°C with holding time 10, 20 and 30 hours (Fig. 3), at 1445°C with holding time 30 hours and other group of specimens was fired at 1430°C in a tunnel kiln. The heat-up time in the laboratory kiln was 12 hours. The specimens fired at isothermal dwell of 10 and 20 hours were after removal from the kiln placed in a drier with the temperature 220°C where they were slowly cooled which has a great influence on the final mineralogical composition of the silica bricks [3]. Specimens fired at isothermal dwell of 30 hours were left to cool slowly in the kiln as it was losing heat.



Fig. 3 Specimens before and after firing, fire 1, 2, 3

TABLE II
 LIST AND IDENTIFICATION OF FIRE

Number of fire	Fire characteristics	Firing equipment
1	1415°C/10 hours	laboratory furnace
2	1415°C/20 hours	laboratory furnace
3	1415°C/30 hours	laboratory furnace
4	1445°C/30 hours	laboratory furnace
7	1430°C/90 hours	Industrial tunnel kiln

C. Methods

Even though silica bricks have been used for many years, their international standardization has not received much attention. There are, however, several standards which

characterize silica bricks that apply to products for the coke and glass industries:

- DIN 1089-1 (1995) is an internationally recognized standard concerning the use of silica bricks in the coke-making industry.
- The ASTM C416 standard is used for silica bricks applied in glass industry (especially in the U.S.). It divides materials into two groups depending on a parameter called flux factor (FF). Group A contains materials with $FF \leq 0.5$. Materials in Group B have $FF > 0.5$. Flux factor is defined as the percentage of $Al_2O_3 + 2(Na_2O + K_2O)$.
- ISO EN 10081-1:2003 defines insulating silica bricks, where silica with $SiO_2 \geq 93$ mass-% is designated as SL93. [6]

Our study uses the following analytical methods. Determination of bulk density, apparent density, apparent porosity and water absorption was performed by the well-known hydrostatic gravity method (ČSN EN 993-1 standard). Apparent porosity and pore size distribution were determined using high pressure porosimetry on Thermo Finnigan POROTEC equipment, Pascal 140–240 type. Quantitative elemental analysis was performed by wavelength-dispersive X-ray spectroscopy (WDXRF) using the SPECTROSCAN MAKC-GV instrument equipped with the QUANTITATIVE ANALYSIS software. Samples were analysed in the form of fused beads.

Powder X-ray diffraction analysis was conducted on Bruker D8 Advance diffractometer equipped with a Cu-anode, 1-D position sensitive detector and variable divergence slits at convention Bragg-Brentano para focussing $\Theta - \Theta$ reflexion geometry. Step size – $0,02^\circ 2\theta$, time per step – 188s, angular range $6-80^\circ 2\theta$. Quantitative phase analysis was conducted by the Rietveld method. The amorphous phase contents were quantified using the addition of 20 mass % of fluorite (CaF_2) as an internal standard [5]. The measured data were processed using Diffrac plus and Toaps 3 software.

IV. RESULTS AND DISCUSSION

During the time-consuming research, a number of laboratory tests were performed whose goal was to determine the influence of granulometry and method of mineraliser homogenisation on the utility properties of silica bricks which directly affect the resistance of the material to corrosion and thus also their life-cycle in the structure where they are applied.

Apparent density and apparent porosity values were determined using hydrostatic gravity test and high-pressure mercury porosimetry. The nature of the pore structure of the material is (more or less) influenced by the intrusion of undesirable, mainly alkaline, oxides into the structure of the silica ceramic body where they function as melting oxides and shorten the life of the material.

TABLE III
PHYSICAL MECHANICAL PROPERTIES

Formula	Absorption [%]	Bulk density [kg·m ⁻³]	Apparent density [kg·m ⁻³]	Apparent porosity [%]	Compressive strength [MPa]	
A	1	9,3	1847	2 308	17,7	23,5
	2	9,8	1864	2 302	18,5	29,8
	3	9,8	1893	2 298	18,3	28,6
	4	10,7	1849	2307	19,8	26,4
	7	8,7	1926	2299	16,7	42,6
B	1	8,6	1926	2 315	16,7	45,4
	2	8,5	1922	2 309	16,4	47,5
	3	8,7	1924	2 307	16,7	44,7
	4	10,1	1908	2314	19,0	33,7
	7	8,6	1957	2323	16,6	55,3
C1	1	9,1	1911	2 318	17,3	41,1
	2	8,9	1909	2 308	17,0	43,2
	3	9,0	1913	2 309	17,2	41,9
	4	10,2	1899	2312	19,1	34,5
	7	8,5	1948	2312	16,4	48,1
C2	1	8,9	1915	2 314	17,2	38,3
	2	8,9	1916	2 308	17,1	39,7
	3	8,9	1912	2 306	17,1	41,8
	4	9,9	1899	2310	18,7	33,0
	7	8,5	1945	2303	16,3	47,3
D	1	9,2	1898	2 314	17,6	34,4
	2	9,1	1897	2 308	17,3	34,3
	3	9,1	1888	2 302	17,3	31,4
	4	10,1	1892	2307	18,9	30,2
	7	8,4	1949	2295	16,1	47,2

Silica ceramic body only contains a minimum number of closed pores. The pore structure of silica bricks is open and it can be presumed that the average pore size is one of the important parameters for assessing the durability of the material [4]. Compressive strength is also important for the use of silica bricks in the construction of thermal aggregates.

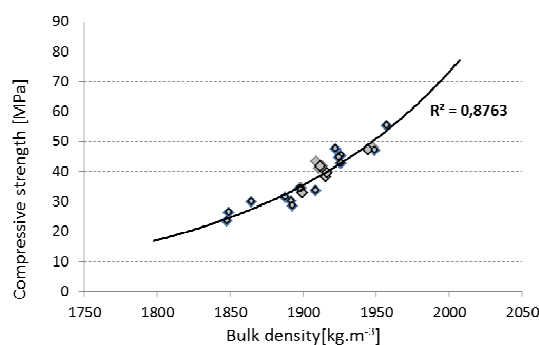


Fig. 4 Dependency of compressive strength on bulk density

With the increase of bulk density by $100 \text{ kg}\cdot\text{m}^{-3}$, compressive strength of the silica refractory rose by more than 100%, from 23 to 55 MPa. Apparent porosity ranged between 16 and 20%. The following figure shows the necessity of using a mineraliser, Fig. 5. The formula which does not contain a mineraliser, formula A has the highest apparent porosity at all firings. It also appears that apparent porosity of the products is

most influenced by the firing length. The firing of specimens in the industrial kiln has brought the lowest porosity of the ceramic body. The firing temperature 1445°C is too high for the production of silica bricks; see firing at 1445°C with isothermal dwell 30 hours.

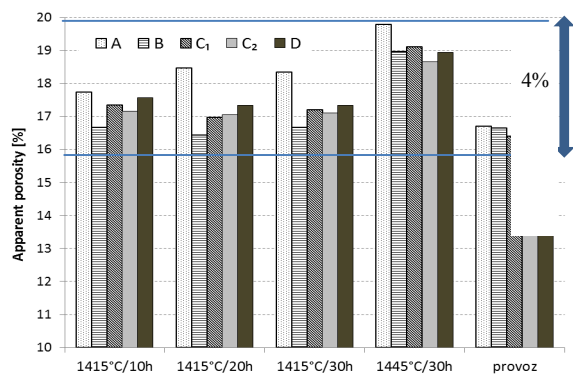


Fig. 5 Dependency of apparent porosity on firing temperature and mineraliser used

Corrosion resistance is influenced mainly by apparent porosity of the material and its bulk density. An important parameter is also its mineralogical composition. A low content of unconverted quartz (α -quartz) is automatically presumed in silica materials. However, tridymite content is equally important. A high tridymite content and low unconverted quartz content is a guarantee of small changes in the volume of silica bricks during the operation of the thermal aggregate where it has been used. A high tridymite content is another condition for long service life of the material in the structure which faces high temperatures.

The influence of isothermal dwell during firing and the influence of the granulometry of the used Fe-mineraliser on the mineralogical composition of the silica bricks is shown in the following table and Fig. 6.

TABLE IV
MINERALOGICAL COMPOSITION, 1415 °C

Formula, Soakingtime	C [%]	T C ₁ [%]	T F ₁ [%]	T [%]	Q [%]	Glass [%]
A 10 hour	72,2	0	9,6	9,6	2,6	15,7
A 30 hour	64,3	3,5	12	15,5	0,6	19,7
B 10 hour	68,3	1,7	9,6	11,3	2,7	17,7
B 30 hour	66,9	7,6	12,5	20,1	0,9	12,1
C1 10 hour	70,1	2,3	11,1	13,4	2,7	13,8
C1 30 hour	60,2	5,2	16,8	22	0,6	17,2
C2 10 hour	60,7	3,1	7,9	11	2	26,3
C2 30 hour	62,7	2,9	17,3	20,2	0,9	16,2
D 10 hour	74,4	3,9	7,4	11,3	2,6	11,6
D 30 hour	60,3	3,4	13	16,4	0,6	22,8

C- cristobalite, T- tridymite (C₁, F₁ modification), Q- quartz

The determined content of unconverted quartz does not exceed 2,7 mass %. The specimens are characteristic by their broad range of glass phase content from 11,6 to 26,3%. Glass phase content is strongly influenced by mineraliser and the length of isothermal dwell. Specimens where a mineraliser

was not used exhibit at extended isothermal dwell a higher content of glass phase, much like those samples where coarser-grained mineraliser was used (formula D). The reason for the increased glass content in the formula containing mineraliser ground under 50 μ m and homogenised in a dry mixture for 24 hour is probably the even distribution of fine particles of the Fe-mineraliser (flux) in the mixture, the reduction of viscosity of glass phase during firing and faster crystallisation of cristobalite. Cristobalite does not subsequently crystallise into tridymite during cooling. This technology of homogenisation has appeared as suitable for accelerated formation of tridymite.

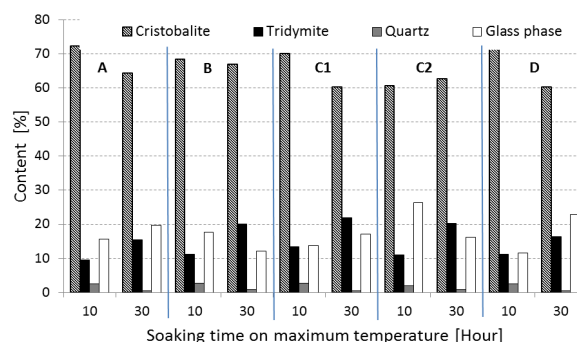


Fig. 6 Mineralogical composition of silica during firing at 1415°C

As has been said above, the presence of tridymite in a silica ceramic body is desirable due to small changes in volume of the material. These volume changes are the lowest of the volume changes of materials contained in silica bricks (cristobalite, tridymite, α -quartz, glass phase). Tridymite content is influenced by the technology of mixture preparation, use of Fe-mineraliser and especially the firing length of the final products [7]. During firing, cooling of the material is crucial for the formation of tridymite and it should be, in an ideal case, controlled down to temperatures of about 150°C.

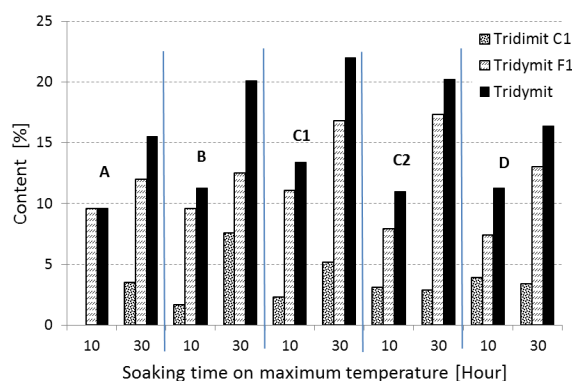


Fig. 7 Portion of C1 (monoclinic) and F1 (triclinic) modifications in the total content of tridymite in firing at 1415°C

Two phase modifications of tridymite were identified in the specimens (C1-high, F1-low), Fig. 7. The obtained data indicates the necessity of using a Fe-mineraliser during

production (high tridymite content). The positive influence of the length of isothermal dwell on the formation of tridymite was proved.

The lifespan of silica bricks in the structure of a thermal aggregate is influenced by not only its mineralogical composition, apparent porosity, bulk density and strength but also by the characteristics of the pore structure of the material. Silica ceramic body only contains a minimum number of closed pores. The pore structure of silica bricks is open and it can be presumed that it is one of the important parameters for assessing the durability of the material, Fig. 8. Open porosity enables the intrusion of undesirable, mainly alkaline, oxides into the structure of the ceramic silica body during operation of the thermal aggregate where they function as melting oxides and shorten the life of the silica bricks in the aggregate.

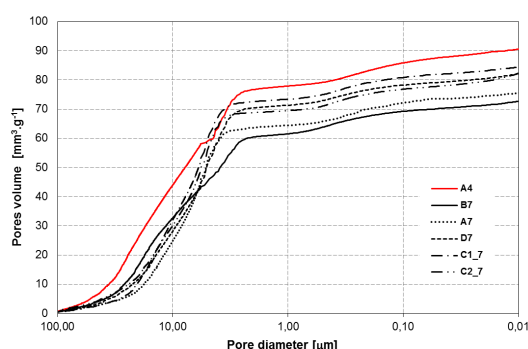


Fig. 8 Pore diameter distribution

The oolitic structure characteristic for silica bricks is visible in Fig. 9. The internal structure of the silica bricks where no mineraliser was used has lower compressive strength which is connected with a lower glass phase content whose formation was not assisted by the Fe-mineraliser during firing. Due to a lower content of glass phase, a lower content of tridymite had formed, which reduces compressive strength.

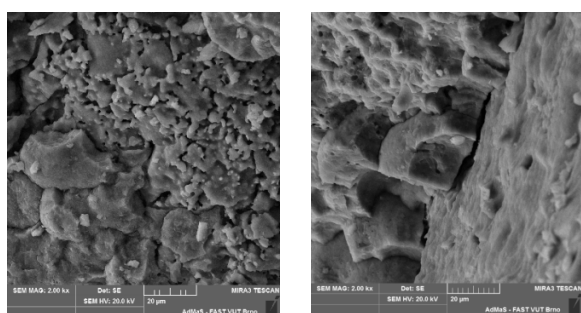


Fig. 9 Internal structure of silica refractory, magnified 2000x.
Formula A1 on the left, formula C2_3 on the right

V. CONCLUSION

The study discusses the influence of Fe-mineraliser on the utility properties of silica bricks which have a direct influence on its durability in the structure of an oven. It was confirmed that.

- extending isothermal dwell during silica brick production

(extending heat exposure during firing) contributes to a greater tridymite content.

- the presence of an Fe-mineraliser in the formula is necessary during silica production; it has a positive influence on the apparent porosity of the material (Fe-mineraliser reduces porosity) and has a positive influence on the formation of tridymite (Fe-mineraliser increases tridymite content).
- firing temperature 1445°C and higher is not suitable for firing dense silica.
- firing time has no influence on open pore diameter, only on their amount.

The study also examines the influence of the granulometry of the Fe-mineraliser used in the mixture for silica brick production. The study proved the positive influence of the finely ground mineraliser (below 50 µm) on the formation of glass phase during silica bricks firing and thus also on the amount of tridymite being formed. However, the use of such finely ground mineraliser increases the porosity of the material. The optimal grain size of Fe-mineraliser is up to 200 µm; further decrease in grain size of the Fe-mineraliser (further milling) leads to an undesirable increase in apparent porosity in the material.

ACKNOWLEDGMENT

Thanks are due to Alfa TAČR TA02010084 Development of Silica Materials with Optimized Properties with Emphasis on Corrosion Resistance project.

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