Original Paper

Spinel bricks for highly stressed roofs in glass melting furnaces

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New challenges are raised to the refractory materials in the crown and superstructure of oxy-fuel fired glass melting furnaces in comparison to air-fuel fired glass melting furnaces. In glass melting furnaces which are oxy-fuel fired the water steam partial pressure above the melt increases very strongly. In the case of soda-lime-silica glass melts together with the water steam partial pressure the alkaline hydroxide partial pressure increases with a factor of three in comparison to an air-fuel firing system. This leads to an aggressive action on the refractory lining in the crown and superstructure. After extensive thermodynamic calculations and laboratory tests a pure spinel refractory material ($MgO \cdot Al_2O_3$) was developed for the application in the crown and superstructure of oxy-fuel fired glass melting furnaces.

The chemical and physical properties as well as the results of corrosion tests under oxy-fuel conditions of this direct-bonded fused spinel material will be discussed. Because of the high corrosion resistance to alkaline attack and the excellent behaviour of the creeping under load even at a temperature of 1650 °C, this spinel material can be proposed for the successful application as crown and superstructure refractory for oxy-fuel fired glass melting furnaces.

Spinellsteine für hochbelastete Glaswannengewölbe

Bei der Anwendung der Oxy-Fuel-Technik zur Glasschmelze ergeben sich im Gegensatz zur Luft-Brennstoff-Feuerung erhöhte Belastungen für die feuerfesten Werkstoffe, die im Gewölbe und Oberofen eingesetzt werden. So nimmt bei Oxy-Fuel-Feuerung der Wasserdampfpartialdruck im Oberofen stark zu. Bei der Schmelze von Kalk-Natronsilicatgläsern erhöht sich mit dem Wasserdampfgehalt der Alkalihydroxidpartialdruck um den Faktor 3 im Gegensatz zu einer Brennstoff-Luft-Beheizung. Diese Tatsache führt zu chemischen Reaktionen mit den feuerfesten Steinen im Gewölbe und Oberofen. Nach ausgedehnten thermodynamischen Berechnungen und entsprechenden Laborversuchen wurde ein stöchiometrisch zusammengesetzter Spinellstein ($MgO \cdot Al_2O_3$) für die vorgenannten Anwendungen entwickelt. Dieser Steintyp besteht aus einem schmelzgegossenen Spinellkorn mit einem hohen Anteil an Direktbindung.

Die chemischen und physikalischen Eigenschaften des Spinellmaterials sowie die Ergebnisse von Korrosionsversuchen unter Oxy-Fuel-Feuerungsbedingungen werden vorgestellt. Die gute Korrosionsbeständigkeit gegenüber Alkaliverbindungen und das ausgezeichnete Druckfließverhalten selbst bei einer Temperatur von 1650 °C führten dazu, den Spinellstein zum Einsatz im Gewölbe und Oberofen von oxy-fuel-befeuerten Glasschmelzwannen vorzuschlagen.

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1. Introduction

For many years the application of magnesite or spinel bricks in the aluminium, cement and glass industries has been well known. The literature [1 to 3] gives an overview about the advantages and disadvantages of these bricks. Their weakness is caused by the silicate bonding phase of the periclase grains. On account of the instigation of the industries mentioned above a very pure magnesia-alumina spinel brick with a high portion of direct bonding was developed.

During the production of high-quality aluminium metal, the used tank-lining bricks may not contain oxides which are reducible by the liquid aliminium. The melt exhibits a very low viscosity. Therefore, the refractory bricks must have a texture which cannot be penetrated by the liquid metal. Application laboratory tests and the results received from industrial practice of the new spinel bricks led to satisfactory answer for the customers.

In the rotating kilns of the cement industry the oxidation of the magnesia-chromia bricks leads to the formation of alkaline and alkaline earth chromates. The periclase bricks show the well-known sulfate bursting [4]. Also in these kilns spinel bricks were introduced successfully. In the zone of direct contact between the cement raw materials and the spinel bricks a reaction forming

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Table 1. Chemical and physical data of Spinel SP75AB

Al_2O_3		74 wt%
MgO		26 wt%
SiO_2		< 0.2 wt%
Fe_2O_3		< 0.1 wt%
bulk density		3.0 g/cm^3
apparent porosity		14 vol.%
cold crushing strength		50 N/mm^2
refractoriness under load		> 1700 °C
thermal expansion		0.85 % at 1000 °C
thermal conductivity at	800 °C	4.2 W/(mK)
	1000 °C	3.8 W/(mK)
	1200 °C	3.7 W/(mK)
thermal shock resistance:		medium

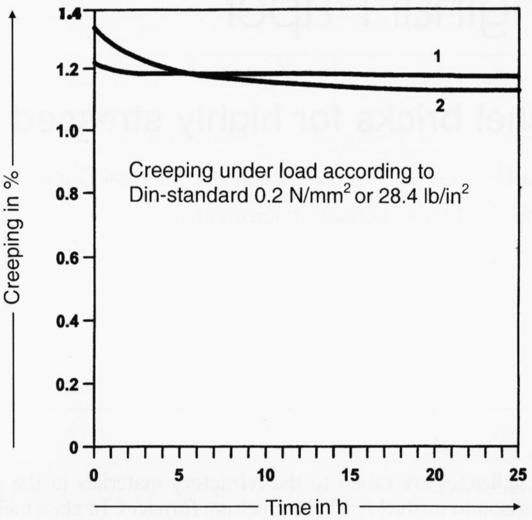


Figure 1. Creeping under load according to DIN-standard [7] of SP75AB as a function of time at different temperatures; curve 1: 1500 °C, curve 2: 1650 °C.

calcium aluminate compounds takes place. But this slagging reaction turns out slowly and without a spalling effect.

In the glass industry spinel bricks containing grains of electrofused spinel with a high portion of direct bonding are installed in the middle part of the regenerative chambers. To suppress the attack of sulphur trioxide and sodium hydrogen sulfate, the bricks neither may have periclase grains nor a silicate bonding phase.

2. Chemical and physical properties of the spinel bricks

As mentioned before the demands of the customers are well defined. They require magnesia-alumina spinel bricks with a low content of silica and iron oxide and a nearly complete direct bonding of the spinel grains. As the spinel grains must exhibit a low porosity only electrofused spinel was used. Furthermore, the formation of the direct bonding requires high firing temperatures during the burning process.

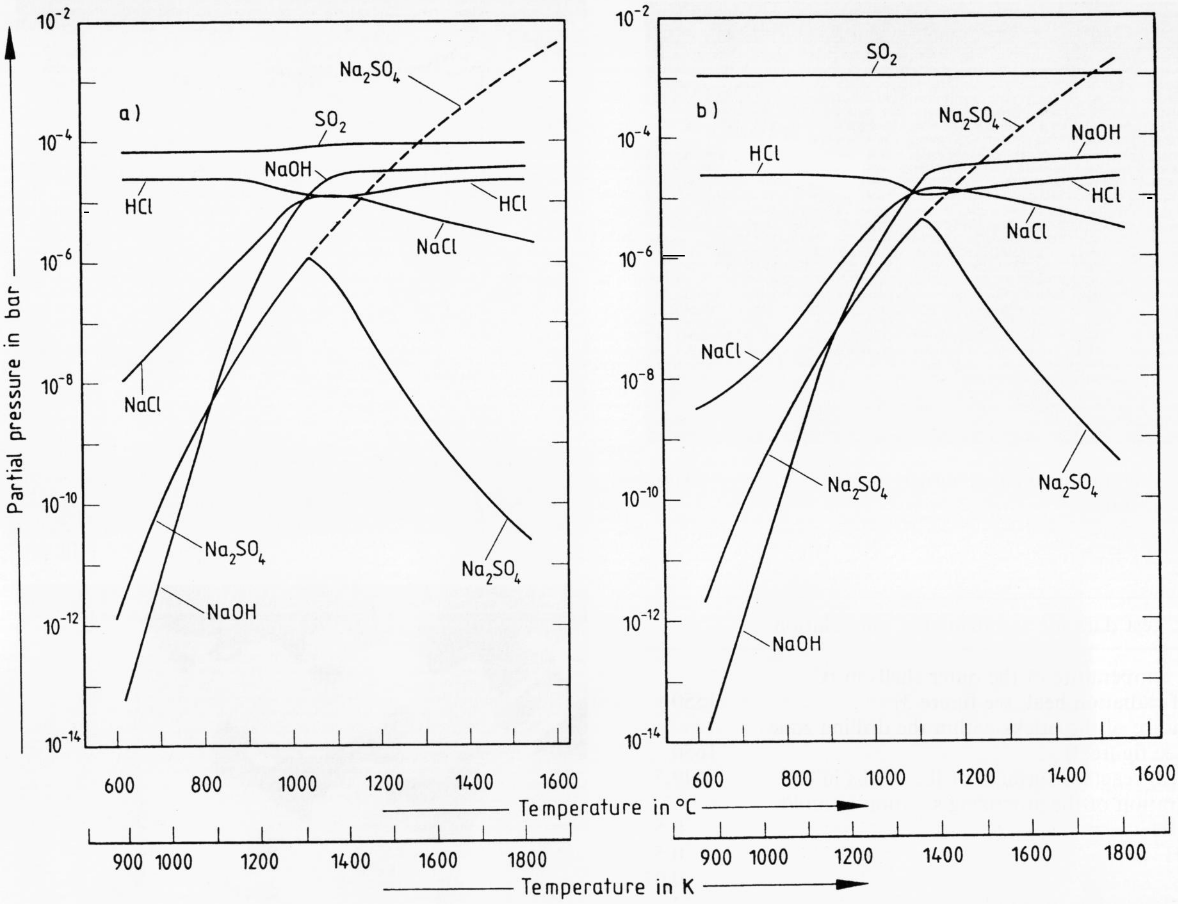
Table 1 gives the chemical and physical properties of the bricks produced. The chemical analysis and the X-ray powder diffraction show a stoichiometric composition without any surplus of magnesia or alumina. The characteristic structure of the bricks will be obtained by a well-defined grain size distribution and the high firing temperature. For the application in the superstructure or roof in a soda-lime-silica glassmelting furnace they have to be resistant to alkaline hydroxide vapours and also to silica-containing water vapour [5 and 6]. Besides, a very low creeping under load is expected.

At first the creep under load particularly at very long testing time shall be presented. The employed test temperature amounted to 1600 °C corresponding to the temperature of the hot face of the roofs in the melting tanks. The load was chosen according to DIN/EN 993-9 [7] with 0.2 N/mm^2. Figure 1 shows the diagram of the creep under load of these spinel bricks. Up to 1500 °C the bricks have a linear expansion of 1.2 %. At this temperature the test samples shortly showed a very low creeping as a function of time. The final values were reached after 2 to 3 h and did not change anymore within 500 h testing time. The presented values for creep under load were confirmed by the research laboratory of a large European flat glass producer. That research laboratory also confirmed the analogous behaviour of silica bricks and the presented spinel bricks.

3. Laboratory corrosion tests

The material mentioned before is to be used as well in air-fuel as in oxygene-fuel fired glass melting tanks. Therefore, it is necessary to compare both firing types and the composition of the different waste gases above the melt (fusion) of soda-lime-silica glass. Figures 2a and b show the composition of waste gases for a gas-air and fuel-air fired flat glass tank as a function of temperature [8]. According to this diagram the vapour pressure of sodium hydroxide amounts to $5 \cdot 10^{-5}$ bar at 1500 °C. The vapour pressure of water in the waste gas (600 °C) was measured with 0.143 bar for gas-air firing and with 0.101 bar for a fuel oil-air firing. For a given batch composition the pressure of water vapour above the glass melt is a function of the C/H ratio of the combustibles [methane: C/H = 75 %/25 %; fuel oil: C/H = (82 to 87 %)/(10.8 to 6.5 %)]. For the combustion with pure oxygen the partial pressure of water vapour increases by a factor of three.

D. M. Sanders and H. A. Schaeffer in their fundamental studies have shown [9] the relationship of the va-



Figures 2a and b. Partial pressure of waste gas components versus temperature for different glass melting furnaces [8]; a) glass melt 1 (gas-air fired), b) glass melt 2 (fuel-oil air fired).

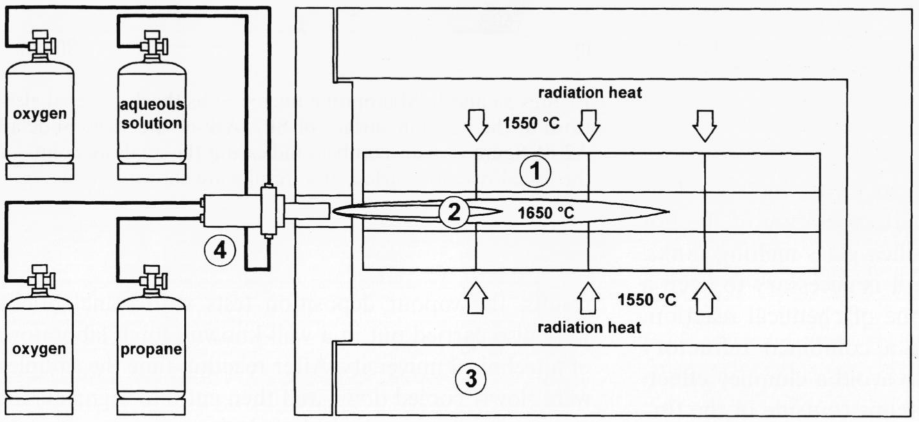


Figure 3. Schematic drawing for the test furnace; 1: test bricks, 2: oxy-fuel flame, 3: furnace, 4: burner.

porization of alkaline hydroxide, the vapour pressure of water above the melt and the reaction time. Considering these results one can determine for oxy-fuel firing a vapour pressure of sodium hydroxide which is two or three times higher than for an air-fuel (combustible) firing ($P_{NaOH} \approx 10^{-4}$ to $5 \cdot 10^{-4}$ bar). These values are in accordance with measurements in practice.

Different experimental facilities were chosen to simulate the chemical reactions between the furnace atmosphere and the refractory materials. Figure 3 presents the installation which was constructed by Vesuvius VGT-DYKO for testing the materials. In an air-gas fired furnace refractory bricks (big single ones or combinations of usual sizes) with a central drilling zone of 50 mm (di-

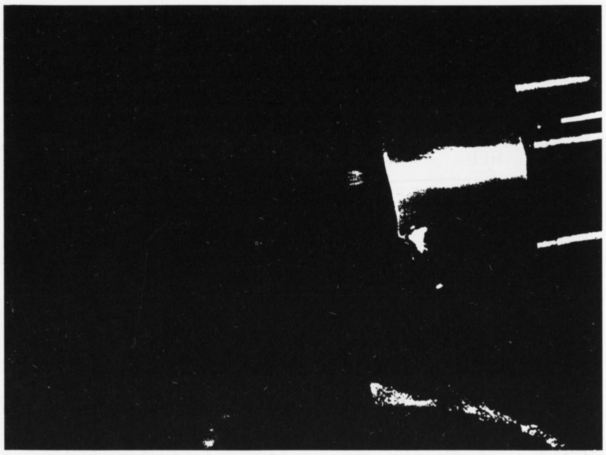


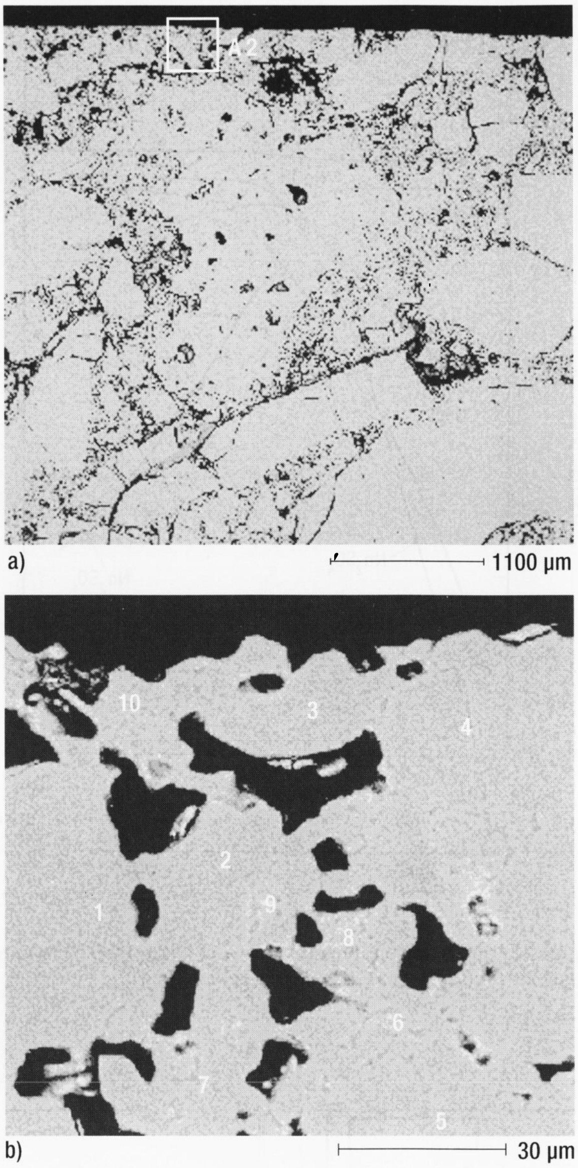
Figure 4. Nebulizing oxy-fuel burner; burner diameter = 50 mm, depth = 33 mm.

Table 2. Test data for atomizing the salt solution

furnace temperature of the outer shells in °C (zone of radiation heat, see figure 3)	1550
temperature of the bricks within the drilling zone in °C (see figure 3)	1650
cylindrical reaction surfaces of the bricks in cm^2	549.5
concentration of the atomizing solution in mol/l	
NaOH	0.5
KOH	0.5
SiO_2	0.07
vapour deposition time in h	32
reaction time in h	96
sample surface attacked by the solution in $mg/(cm^2h)$	
NaOH	34
KOH	49
SiO_2	7
velocity of the waste gases in cm/s	≈ 25
gas flow of propane and air in l/h (oxidizing atmosphere)	1754

ameter) were installed and heated up to 1600 °C. This temperature is equivalent to the temperature of the hot face of the roof of soda-lime-silica glass melting tanks. To receive reproducible results, it is necessary to keep a constant temperature in the zone of chemical reaction. The joints of single bricks in a combined refractory block were filled with mortar to avoid a chimney effect. By help of an oxygen/propane flame (outside of the furnace) a solution which contains sodium and potassium hydroxide as well as sodium and potassium silicate is injected into the drilling. The silicates were added to the solution on request of some customers.

The construction of the burner is very important. Before reaching the reaction zone the solution has to be totally nebulized in the oxygen-propane flame. The occurence of droplets in the flame cannot be tolerated. Figure 4 presents the nebulizer and table 2 shows the test data for the atomized solution. To confirm the obtained results, the vapour deposition tests with spinel bricks were also carried out in a well-known Dutch laboratory of a technical university. After reaction time the samples were slowly cooled down and then cut into segments for chemical and mineralogical analysis.



Figures 5a and b. Microprobe micrographs (backscattered electron) of the reaction surface of SP75AB; a) overview, b) detail A2 of figure a) with numbers indicating the analysis points of the tested reaction surface (the results are shown in table 3).

4. Results of the laboratory tests

By macro- and microanalysis with reflecting and transmitting light one cannot observe any changes of the bricks tested. But the analysis of the single zones with the electron scanning microscope showed unimportant chemical reactions. These are points of about 10 to

Table 3. Results of microprobe analysis (in wt%) of analysis points in figure 5b

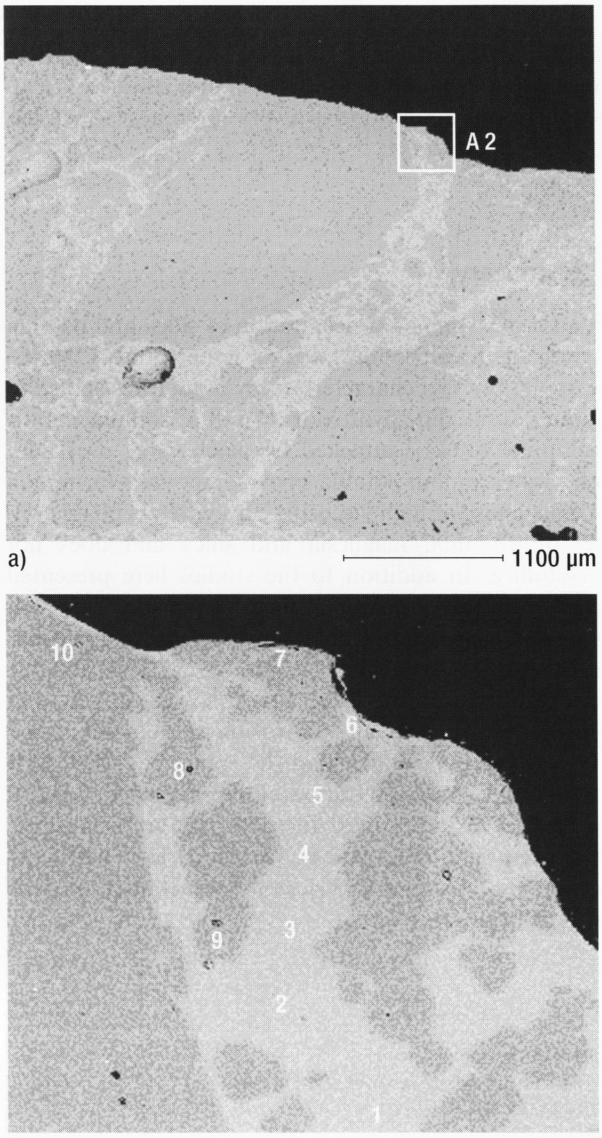
	point 1	point 2	point 3	point 4	point 5	point 6	point 7	point 8	point 9	point 10
MgO	24.9	24.8	25.6	25.1	24.6	15.5	13.7	13.0	9.3	8.7
Al_2O_3	75.1	75.1	74.4	74.9	75.4	76.1	73.0	72.2	62.0	59.5
SiO_2						7.0	11.2	11.9	23.3	25.8
K_2O						0.8	1.2	1.6	2.5	2.8
CaO						0.6	0.9	1.4	1.8	2.2
Na_2O									1.2	1.0

20 µm elongation between the spinel grains; i.e. the so-called filler material (fine grains) has reacted. The diameter and the number of these inclusions decrease rapidly from the reaction surface to the interior of the sample, and after 3.5 mm from this surface they diminish totally or they are too small to measure.

Figures 5a and b show sections and analytical results (see table 3) of the reaction surface. One can see an enrichment with K_2O, Na_2O and SiO_2 in the filler material. These oxides react with the alumina of the spinel forming a vitreous phase. This reaction takes place only in the presence of a high concentration of silica. Pure alkaline hydroxide vapours do not react. Because of the higher vapour pressure of potassium hydroxide the tested samples present higher concentrations of potassium oxide than of sodium oxide. The surface of the spinel bricks which is in contact with the furnace atmosphere also pointed out few similar tiny spots with an analogous composition to those of the reaction surface, but the concentrations of sodium and potassium oxide and silica are ten to two times, respectively, lower than in the reaction sections.

These results were confirmed by the research institute of the university mentioned before.

To study the influence of higher silica concentrations in the waste gas, a spinel brick was attacked by batch carry over for 70 d at a temperature of 1500 °C. This test was carried out in a melting tank of soda-lime-silica glass. During the slagging reaction a vitreous phase is formed in which the spinel is partially solved (figures 6a and b). The reaction takes place in the filler materials between the spinel grains, but no recrystallization in the alumina and silica enriched glass could be detected by microprobe analysis neither in the upper reaction zone nor in the interior of the bricks (see table 4).



Figures 6a and b. Microprobe micrographs (backscattered electron) of the reaction surface of SP75AB after a 70 d attack at 1500 °C caused by a high batch carry over; a) overview, b) detail A2 of figure a) with numbers indicating the analysis points of the tested reaction surface (the results are shown in table 4).

5. Industrial application

On account of the good laboratory results the bricks are being tested in the glass industry. At first the spinel bricks were installed in the end wall of a big flat glass melting furnace. In this melting area one can find a very high concentration of dust from fine-grained particles of the batch. Now, the end wall has been in operation for 16 months without any complaint. Further on the spinel bricks were installed in the roof of a melting furnace for

Table 4. Results of microprobe analysis (in wt%) of analysis points in figure 6b

	point 1	point 2	point 3	point 4	point 5	point 6	point 7	point 8	point 9	point 10
MgO	6.41	6.48	6.47	7.01	7.11	19.60	29.1	28.8	28.8	29.2
Al_2O_3	28.36	26.79	28.51	27.20	27.93	71.54	70.9	71.2	71.2	70.8
SiO_2	53.94	56.50	54.06	55.09	54.47	8.13				
K_2O	0.47	0.54	0.46	0.57	0.44	0.09				
CaO	6.66	5.88	6.01	5.97	6.16	0.65				
Na_2O	4.16	3.81	4.07	4.11	3.89					
Fe_2O_3			0.43	0.05						

the production of water glass. On account of the high concentration of sodium hydroxide and silica in the atmosphere this application is a very severe test which has not been finished yet.

6. Summary

Because of its minor concentration of silica and its high portion of direct bonding (firing temperature 1780 °C) the spinel brick is characterized by a good resistance to vapours of alkaline hydroxide as well as sodium borate. The spinel brick is attacked by batch carry over and/or by water vapour soluble silica compounds forming a vitreous phase of high viscosity. This vitreous phase consists of alumina, magnesia and silica and does not recrystallize. In addition to the studies here presented evaporation tests from a salt melt were made. This melt contained a mixture of potassium and sodium hydroxide. Even with these highly concentrated pure alkaline hydroxide vapours the spinel brick showed no reaction. Considering the presented corrosion resistance and the very low creeping under load the spinel brick SP75AB is qualified for the application in the superstructure and the roof of oxy-fuel fired furnaces melting soda-lime-silica glass or borate glasses. In comparison with corundum, mullite and AZS bricks the spinel brick pointed out no slagging reactions.

7. References

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