

Bonded Refractories for Extreme Conditions in the Top of Regenerators

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The regenerator top, including the top checker layers, crown, and walls, is one of the most stressed parts of a glass melting furnace. Depending on the choice of raw materials, fuel, and operating conditions for the glass production, chemical attack and thermal stress in the top of a regenerator can vary widely. The article reviews the historical developments behind the refractory choice for this section of the furnace. Furthermore, the results of laboratory tests examining refractory corrosion resistance to alkali, carryover, and glass melt attack are reported as well as field trials to evaluate refractory materials for regenerator top applications.

1 Introduction

The regenerator top (Fig. 1) is always one of the most stressed parts of a glass melting furnace. Nowadays, the trend for energy and cost savings in the glass industry simultaneously causes more carryover (in the case of cullet preheating or batch preheating) and/or creates an aggressive atmosphere in the waste gas (in the case of alternative fuel use). Therefore, the refractories used in the regenerator top face significant challenges. In this paper the in service experience and refractory material choice for these extreme conditions are reported.

2 Bonded materials for the top checker layers in the regenerator

2.1 Historical overview from 1940 to 2000

During the 1940s, magnesia bricks found their application in the glass industry, including in the top checker work layers, because fire clay bricks and silica bricks were unsatisfactory for certain highly stressed positions [1–5]. The use of magnesia refractories in the top layers enabled the furnace and checker work campaign life to be extended. The advantage of magnesia is it has a low potential to react with alkalis present in the atmosphere. Therefore, there is no so-

called “alkali bursting” that is common with fireclay and silica bricks. However, because of the basic character of magnesia it reacts with SiO_2 in the carryover to form forsterite ($2\text{MgO}\cdot\text{SiO}_2$), which causes so-called “silicate bursting” [6, 7]. With limited success, countermeasures to circumvent this disadvantage were taken, including:

- Using low iron and high fired magnesia [8, 9].
- Installing modified basic bricks, for example magnesia chromite bricks [10].
- Installing alternative refractories, such as mullite zirconium silicate bricks (e.g., ZRX) [11].
- Modifying the upper surface of the checker brick walls to a rounded or angled shape so the carryover cannot accumulate on the checker bricks [12].

In the 1980s, the first magnesia zircon grade was developed [13, 14]. Zircon (ZrSiO_4) is one of the raw material components and as a result the coarse magnesia grains become protected by a forsterite ($2\text{MgO}\cdot\text{SiO}_2$) and zirconia (ZrO_2) bonding matrix that forms during the brick firing process. Since this advance, magnesia zircon bricks have become the leading choice for top layer checkers if ceramic-bonded refractories are used.

In the case of a higher CaO content in the carryover, the CaO can react with MgO and



Fig. 1 Regenerator chamber with checker work (copyright RHI AG)

the SiO_2 component of forsterite in the magnesia zircon bricks to form low melting Ca- and Mg-silicates (e.g., monticellite and merwinite). Therefore, rebonded fused

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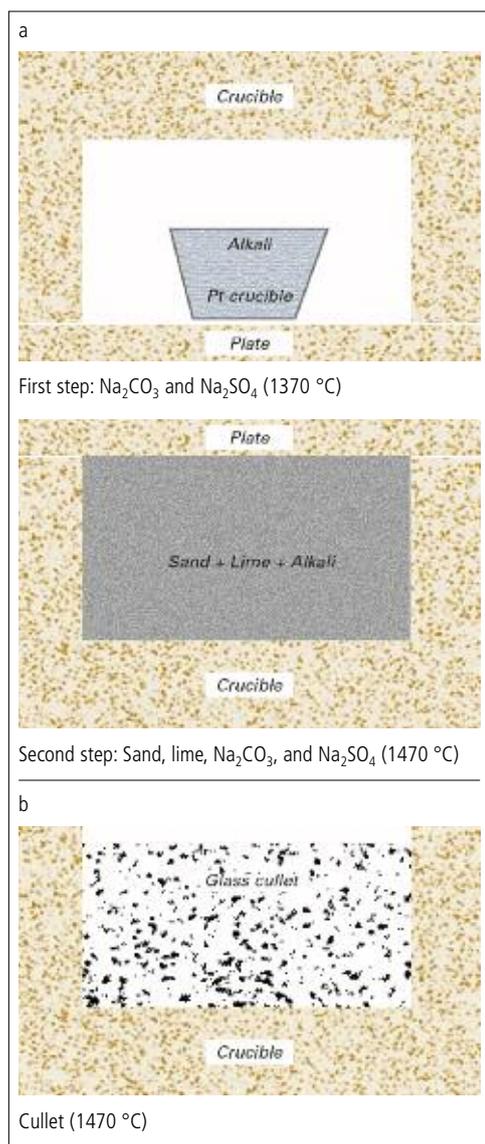


Fig. 2a–b Corrosion tests to examine the attack caused by (a) alkalis and carryover and (b) cullet (copyright RHI AG)

corundum has been used for top layer refractories since 2000. Typically, the fused corundum is inert to alkali attack if the application temperature is over 1350 °C [15, 16]. However, below 1350 °C there is a possibility that corundum will react with alkalis from the waste gas and form β -alu-

mina, which causes a volume increase and results in product failure.

2.2 New challenges for top checker layers in the regenerator

The glass industry is continuously focused on energy savings and improving environmental protection. Furthermore, there is a constant commitment to decreasing production costs. As a result multiple measures have been implemented, such as:

- Increasing the cullet recycling rate.
- Reusing dust from electric precipitators.
- Employing batch preheating and cullet preheating.
- Using alternative energy sources such as petroleum coke.
- Flame optimization to decrease NO_x .

However, all these factors can cause more carryover (in the form of dust or even a higher proportion of fine glass cullet) or/and create an aggressive waste gas atmosphere (e.g., higher vanadium content in waste gas). This article focuses on the carryover attack while the study on vanadium attack caused by petroleum coke was reported in the Industrial RHI Bulletin [17].

2.3 Corrosion tests

To evaluate the corrosion resistance of various refractories, a two-step test was performed to examine the combined attack caused by alkalis and carryover (Fig. 2a). In the first step, a crucible manufactured from the refractory material to be tested was placed over a platinum crucible containing the alkali test media (i.e., Na_2CO_3 and Na_2SO_4) at 1370 °C. In the second step the refractory crucible was subsequently filled with sand, lime, and additional alkali (i.e., Na_2CO_3 and Na_2SO_4) and tested at 1470 °C. A separate test was performed to examine the interaction between the different refractory materials and glass melt (Fig. 2b). In this test the refractory material crucible was filled with cullet and the test was carried out at 1470 °C.

The test results are presented in Fig. 3. The magnesia zircon brick (RUBINAL VZ) was corroded not only by alkali and carryover (Fig. 3a) but also by glass melt (Fig. 3b). It is known that magnesia zircon bricks can be corroded by CaO. The CaO reacts with the SiO_2 present in the brick to form low melting Ca- and Mg-silicates [16]. Following contact with the glass melt, the magnesia grains in RUBINAL VZ were dissolved and washed out.

As a result of alkali attack the rebonded fused corundum (DURITAL K99EXTRA) expanded due to the formation of β -alumina (Fig. 3c). This is why DURITAL K99EXTRA is not recommended for low temperature applications where alkali can condense from waste gas and seriously attack the bricks. The rebonded fused corundum was also dissolved following contact with the glass melt (Fig. 3d).

A zirconia mullite brand (DURITAL AZ58) was developed for top checker layer applications using an optimized raw material concept and production parameters. The corrosion tests showed an improved performance compared to RUBINAL VZ and DURITAL K99EXTRA against alkali attack and dust carryover (Fig. 3e), and especially against glass melt attack (Fig. 3f).

The highest corrosion resistance against alkalis, carryover, and glass melt was demonstrated by the chrome corundum brick (DURITAL RK10) and ceramic-bonded zirconia (ZETTRAL 95CA). Both materials showed minimal interface corrosion (Fig. 3g–j).

2.4 Refractory recommendations for top checker layers

Tab. 1 summarizes the most suitable materials recommended for top checker layers depending on the specific dust situation and waste gas temperature in the regenerator top. In this table “high temperature” refers to a minimum of 1350 °C whilst “lower temperature” indicates in the range of 1300–1350 °C. However, it is important to

Tab. 1 Bonded refractories recommended for the top checker layers operating under different conditions

* indicates the temperatures are only a reference and can change due to other factors (e.g., alkali concentration in the waste gas)

Conditions	Sand Carryover	Sand Carryover with CaO	Fine Glass Cullet	“Worst Case” (Carryover + Cullet)	
High waste gas temperature in regenerator top: >1350 °C *	Magnesia zircon RUBINAL VZ	Rebonded fused corundum DURITAL K99EXTRA	Zirconia mullite DURITAL AZ58	Chrome corundum DURITAL RK10	Bonded ZrO_2 ZETTRAL 95CA
Lower waste gas temperature in regenerator top: 1300–1350 °C *	Magnesia zircon RUBINAL VZ	Zirconia mullite DURITAL AZ58	Zirconia mullite DURITAL AZ58	Chrome corundum DURITAL RK10	Bonded ZrO_2 ZETTRAL 95CA

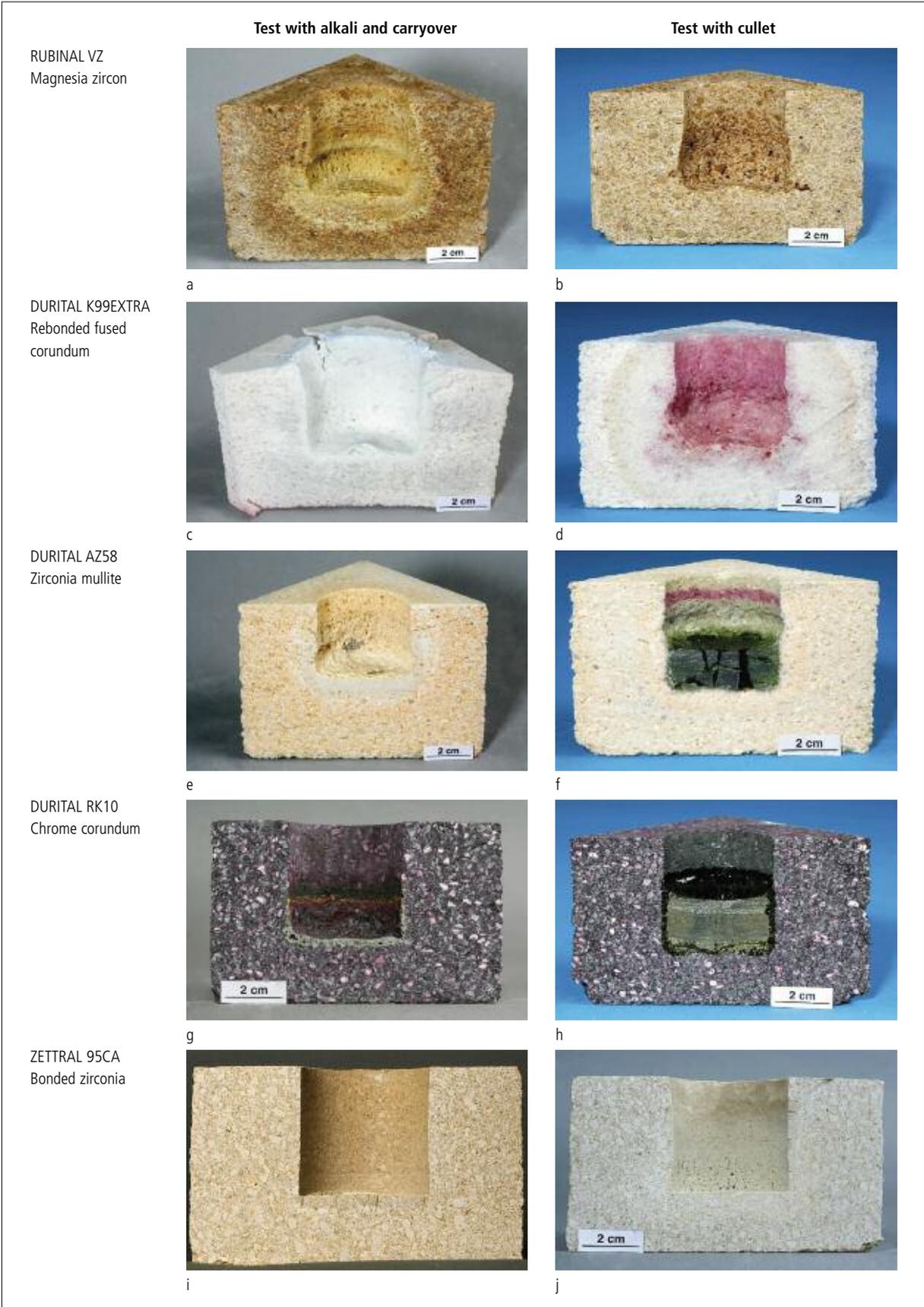


Fig. 3a-j Crucibles after the two-step test with alkali and carryover run at 1470 °C and the test with cullet carried out at 1470 °C (copyright RHI AG)

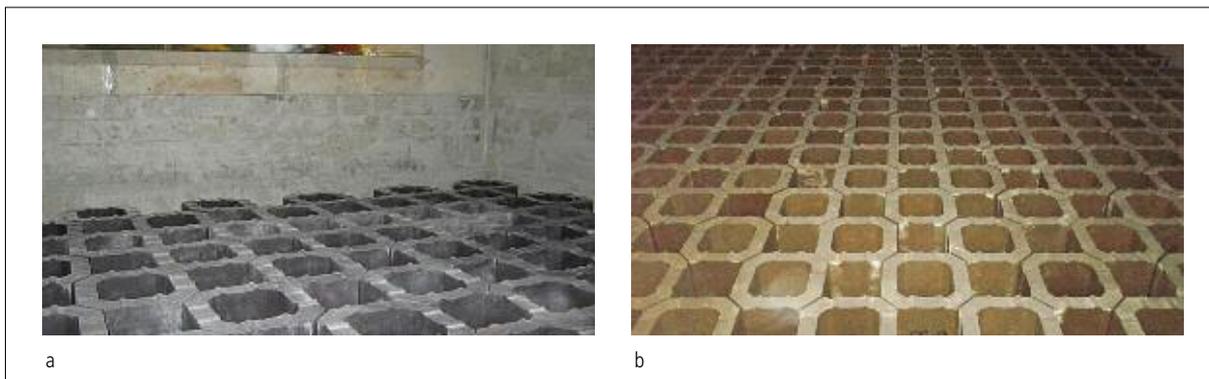


Fig. 4a-b Examples of individual refractory solutions for the top checker layers: (a) top checker layer with chrome corundum (DURITAL RK10) for extremely high carryover and fine cullet in the waste gas and (b) top checker layer with zirconia mullite (DURITAL AZ58) for fine cullet dominating the waste gas (copyright: RHI AG)

stress that the temperatures are only a reference and can change due to other factors (e.g., alkali concentration in the waste gas). In summary, all factors should be considered to select an optimal solution for the top checker layers and because every situation is individual, it is important the refractory supplier determines an individual solution for the customer-specific conditions (Fig. 4).

3 Bonded materials for the regenerator chamber top

3.1 State of the art

As a result of the similar thermal and chemical exposure, the regenerator chamber top has comparable refractory material require-

ments to the top checker layers. However, there are also additional requirements depending on the exact application. For example, since the mechanical stability of the crown is the most critical issue, bricks for this region must have a low creep value. In addition, because of the target wall position it is subjected to a combination of strong physical erosion and chemical attack caused by carryover in the waste gas. Finally, as the separating walls are heated from both sides the thermal load is very high and because in most cases the weight of the crown is loaded on these walls there are additional stresses.

The use of standard silica for the regenerator crown and walls is not appropriate if the

temperature of the waste gas is lower than 1450 °C [18]. While cristobalite is stable above 1470 °C, tridymite is formed below 1470 °C. In standard silica with a lime bonding phase, tridymite is less corrosion resistant than cristobalite against alkali vapour, resulting in standard silica not being suitable for regenerator casing applications where the operating temperature is lower than 1470 °C.

Besides silica bricks, magnesia and high alumina have become established solutions for the regenerator chamber top. There is little controversy in the glass industry regarding the preferred use of magnesia or high alumina bricks [19–22]. In fact both types of refractory can be a good option, with the

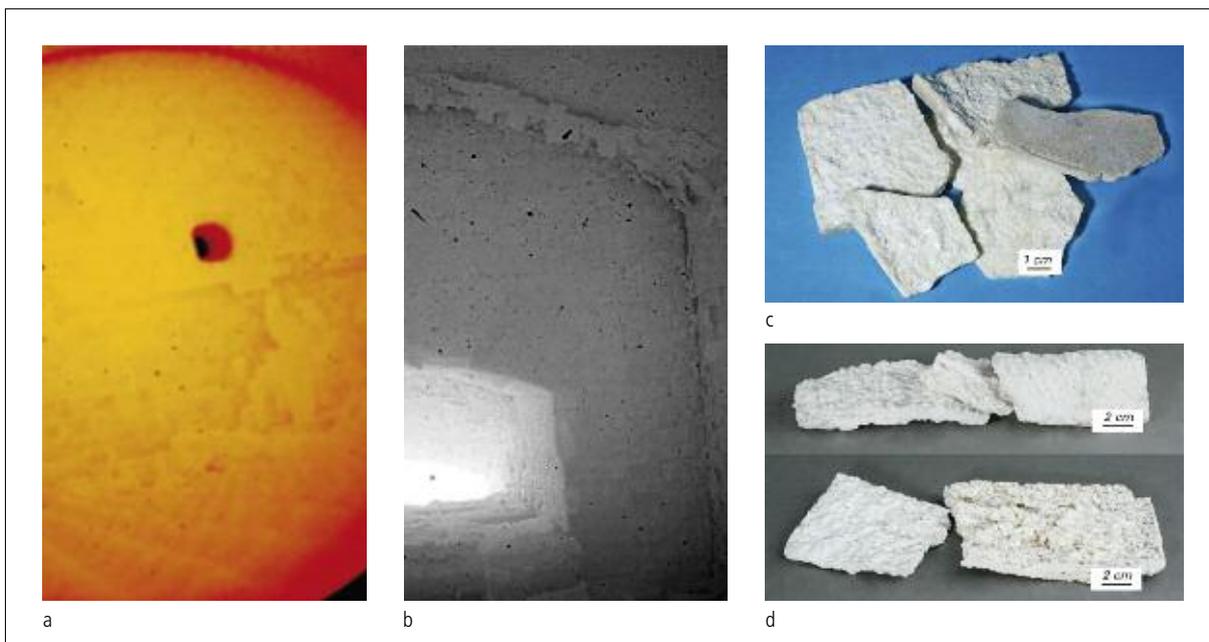


Fig. 5a-d Peeling phenomena occurring if material is used in an unfavourable situation: (a) magnesia bricks in the crown and (b) mullite bricks in the wall; fallen (c) magnesia and (d) mullite pieces collected on the regenerator bottom (copyright: RHI AG)

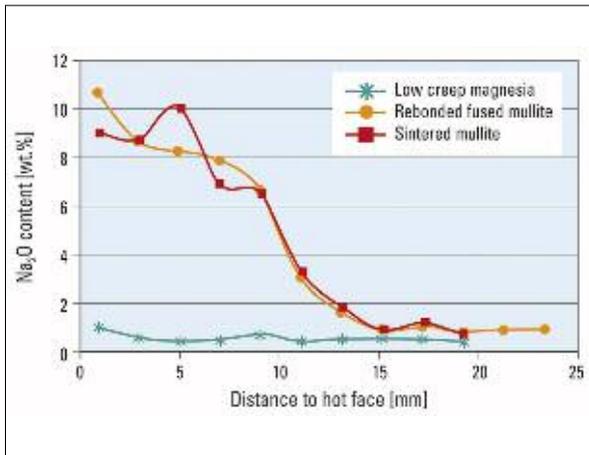


Fig. 6 Na₂O diffusion into mullite and magnesia bricks following a 7-month field test in the regenerator target wall (copyright RHI AG)

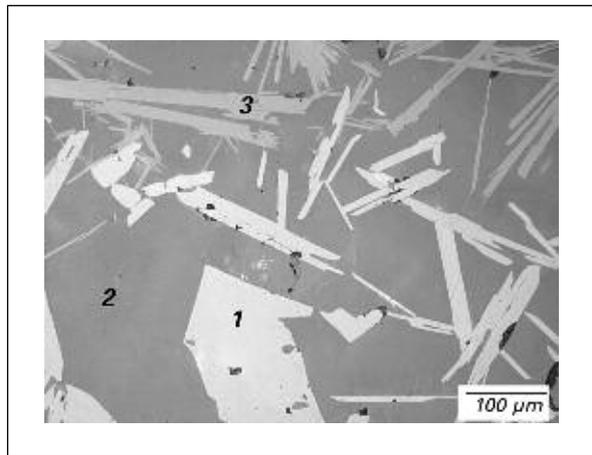


Fig. 7 Microscopic analysis of the sintered mullite brick following a 7-month field test in the regenerator target wall; corundum (1), glassy phase (2), and nepheline (3) are indicated (copyright RHI AG)

choice being highly dependent on the individual situation.

3.2 Magnesia and high alumina refractories

In normal high-grade magnesia bricks with 97 mass-% MgO the grains are bonded with MgO-MgO direct bonding and calcium silicate (Ca₂SiO₄) bonding. The creep resistance of this magnesia brick type is not always sufficient for its application in the crown at high waste gas temperatures. Therefore RHI developed high purity magnesia grades with a low creep value, termed low creep magnesia bricks (e.g., ANKER DG10). The low creep value is achieved through special sintered magnesia with large crystals and optimizing the manufacturing process.

In unfavourable situations peeling can occur, not only with magnesia bricks but also high-alumina refractories (e.g., mullite bricks) (Fig. 5). Magnesia bricks can peel if fine cullet is used to start up the furnace or fine sand is used in the batch. Under these conditions the magnesia can react with the supplied SiO₂ to form a forsterite (2MgO·SiO₂) layer on the brick surface. This is especially the case for the target wall where fine components (i.e., fine cullet and fine sand) from the waste gas “shoot” the bricks surface directly (Fig. 5a–b).

Peeling can also happen if high alumina bricks are used. If the waste gas temperature in the regenerator top is low, alkali attack of the bricks occurs and an alkali-alumina-silicate layer (e.g., nepheline) forms. This layer

can form on all faces of the regenerator top, such as the crown and walls. The nepheline layers can flake off during a temperature change between the waste gas phase and

the air phase (Fig. 5c–d). In a field test different refractory materials were installed in the regenerator target wall. Following a service period of 7 months the Na₂O diffusion

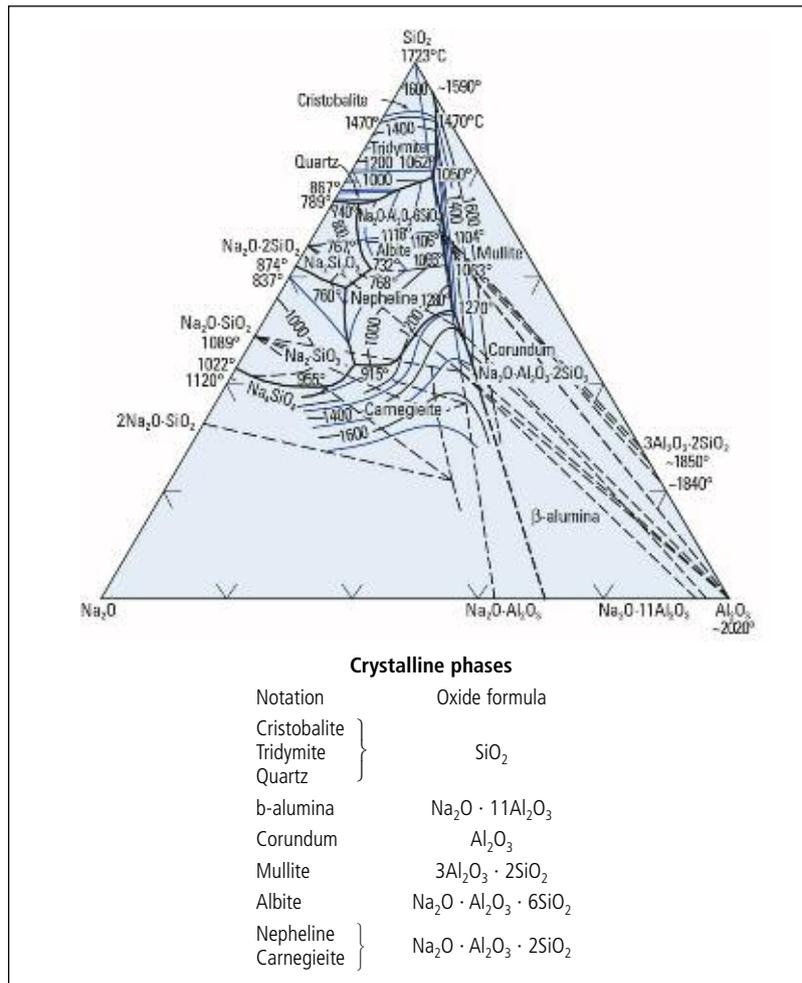


Fig. 8 Phase diagram Na₂O-Al₂O₃-SiO₂

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Tab. 2 Bonded refractories recommended for the regenerator top (i.e., crown and walls)

	Low	High
Alkali in waste gas	>> Low creep magnesia >> Mullite	>> Low creep magnesia
SiO ₂ carryover	>> Low creep magnesia >> Mullite	>> Mullite
Waste gas temperature	>> Low creep magnesia	>> Low creep magnesia >> Mullite

was measured in these samples. Na₂O diffusion into the mullite samples was significantly higher than into the magnesia brick (Fig. 6). While the magnesia brick has a basic chemistry and consequently a high resistance to alkali, the mullite is attacked by alkali to form nepheline and corundum (Fig. 7–8). It is important to select the right material for the top of the regenerator chamber depending on the particular situation. In Tab. 2 the most suitable materials for various operating conditions are recommended.

4 Conclusion

Depending on the raw materials, fuel, and operating conditions in a glass melting furnace, the conditions in the regenerator top can vary quite considerably. It is important to consider all these influencing factors to optimize the refractory selection for this region. With the aid of laboratory tests and field trials at the customer site, tailored solutions for each individual case can be recommended.

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