Refractory lining of carbon-black reactors

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High-quality ceramic materials are required for the refractory lining of reactors for the production of commercial carbon-blacks, The temperatures necessary for the process, which may range up to 1850 °C, depending on process and product, are generated by combusting gas and/or oil, with recycling of preheated air. The following article examines both the various load-exposure zones in the reactor, material selection and the design of the brickwork. The technical data for various brick qualities is shown in tables. Correct installation and commissioning also affect the durability of the refractory lining. Special operating experience is also discussed. The planned increase in process temperatures to above 2000 °C (to permit production of new carbon-black grades) necessitates the development of zirconia-based ceramic materials.

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Introduction

Industrial carbon black is mainly produced by means of the furnace procedure. Continuous operation and high availability of the required reactors very much depend on their lining with suitable refractory products. In addition to the systematic selection of special qualities for the individual furnace areas, an ideal constructional realization of the refractory lining as well as its correct installation are the basis for a long service life. The ceramic application technology must individually be adapted to different carbon black oils, carbon black generator types as well as operational conditions. The main components of a reactor with specific operational demands are the furnace chamber, to which pre-heated air is fed (1), the carbon black oil injection zone (2) and the water injection zone (3). The diagram for this carbon-black reactor type is shown in **figure 1**.

Stress zones

The heat required for the process is generated in the front area of the reactor (1) through the combustion of gas or oil while highly pre-heated air is fed from the downstream recuperator (figure 1). Here, there is an oxidising atmosphere. In the zone after the injection of a specially prepared carbon black oil (2), the fission into carbon and hydrogen under lack of oxygen takes place. In addition to the high thermal stress in this area, the reducing atmosphere, the additives of the carbon black oil, the very high flow rate with the formation of turbulences as well as the resulting difference in gas pressure strongly affect the refractory lining. After the sudden injection of water (3), the process gas temperature drops significantly. However, the stress of the refractory lining is increased through the thermal shock. The size and structure of the individual stress zones may vary and depend on the type of the reactor and the different operational parameters. Some types of carbon black generators are schematically shown in **figure 2**.

Material selection

The refractory material for the lining of carbon-black reactors must fulfil particularly high requirements regarding thermal, chemical and mechanical stresses. For the inner lining as well as for the brick backing and insulation, suitable and well-proven brick qualities based on corundum, sillimanite and chamotte are available. In the zones that are subject to extremely high stresses, a particularly pure corundum brick with more than 99% Al_2O_3 content is necessary. The very high firing temperature of this brick results in a ceramic bond, which in combination with

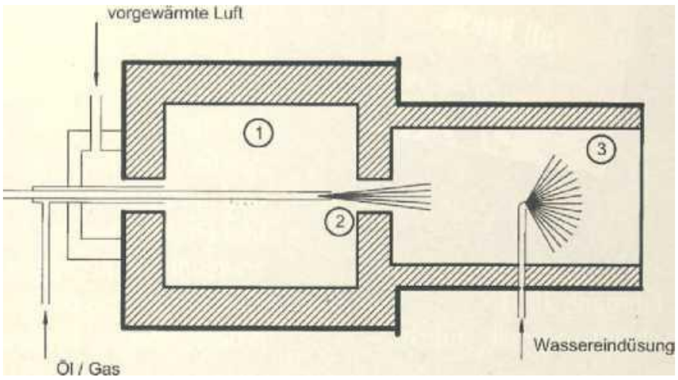

Fig. 1: Diagram of a furnace carbon-black reactor

Fig 2: Carbon-black generator types

the other components added ensures an optimised and durable structure. In **figure 3**, the structural composition of the brick quality Lupudur K99 is shown, which is suitable for this application. This type of brick is characterized by a highly elastic microstructure. The larger tabular alumina grains are built into chains of fine alumina particles. New mineral formations show the highly cross-linked connection. At this point, the relatively good resistance to temperature variations of Lupudur K99 should be pointed out, because this is hard to achieve in bricks with a Al_20_3 content of more than 99%.

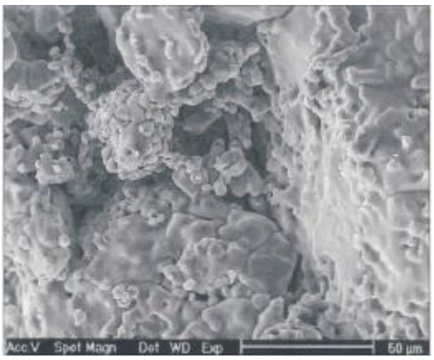

Fig. 3: Lupudur K99 (SEM image, enlargement: 500x)

Not only the pore volume but in particular the form of the pores, as well, play an additional and important role in this context. The melting point of a corundum grain lies at about 2050°C. Considering a reducing gas content after the injection of the carbon black oil as well as the chemical reactions between the additives and the brick surface, fire chamber temperatures of up to 1850°C are controllable. The most important properties of the brick quality Lupudur K99 are listed in **table 1**.

Table 1: Property data for Lupudur K99

Lupudur K99	
Raw material base:	Tabular alumina
Max. application temperature [°C]:	1850°C
Chemical analysis [%]: Al_2O_3	99.3
SiO_2	0.5
F_2O_3	0.1
Bulk density [g/cm^{3}j:	3.2
Open porosity [vol.-%]:	18
Compressive strength |MPa]:	70
Refractoriness under load at (°C):	> 1700
Thermal conductivity according to the hot-wire method [W/mK] at: 600°C	4.00
1000°C	4.35
1400°C	3.86
Resistance to thermal shock according to DIN 51068, part 1 Water quenching method [n]:	17

When choosing the materials for the brick backing, particular attention should be paid to the limit application temperature of the respective quality. For safety reasons, this value

Table 3: Property data for Lupudur FL33-13

Lupudur FL 33-13	
Raw material base:	Hollow corundum spheres
ASTM group:	33
Classification temperature [°C]:	1800°C
Chemical analysis [%]: Al_2O_3	90.0
$Si0_2$	8.0
Fe_20_3	0.2
CaO	-
Bulk density [g/cm^3]:	1.3
Open porosity [vol.-%]:	60
Compressive strength |MPa]:	10
Refractoriness under load at [°C]: Load 0.05MPa	> 1700
Load 0.10MPa	>1700
Load 0.20MPa	> 1650
Thermal conductivity according to the hot-wire method [W/mK] at: 600 °C	1.15
800 °C	1.17
1000°C	1.19
1200°C	1.22
Resistance to thermal shock according to normal stone method cycles [n]: 20 °C - 950 °C - 20°C = 1 cycle in air	22

Table 2: Property data for Lupudur K90 and AK75

	Lupudur K90	**Lupudur AK 75**
Raw material base:	Corundum, mullite	sillimanite
Max. application temperature [°C]:	1750°C	1700°C
Chemical analysis [%]: Al_2O_3	90	75
$Si0_2$	8	25
Fe_20_3	0.15	< 1
Bulk density [g/cm3j:	2.95	2.7
Open porosity [vol.-%]:	19	< 17
Compressive strength |MPa]:	90	>70
Refractoriness under load at (°C):	>1700	1650
Thermal conductivity according to the hot-wire method [W/mK] at:		
600 °C	1.7	1.72
1000°C	2.1	1.76
1400 °C	2.4	1.80
Resistance to thermal shock according to DIN 51068, part 1 Water quenching method [n]:	>60	>30

should be ca. 100°C higher than the calculated boundary layer temperature because of unpredictable peaks in the operational temperature. For the second layer in the highly stressed reactor area as well as the internal lining in the oxidising part of the furnace chamber and after the water injection, corundum or sillimanite bricks with an Al_20_3 content of 90% to 60% can be used depending on the operational parameters. The property data of 2 typical qualities are listed in **table 2**. In case a minimum temperature of the sheet-metal jacket with limited wall thickness is required, a good thermal insulation can already be achieved in the second layer with a hollow sphere corundum quality. It has almost the same Al_20_3 content and almost identical application limits as dense corundum stone but with a 3 times better insulating function. The property data of the hollow sphere corundum variety Lupudur FL 33-13 are shown in **table 3.** Here, we would like to emphasize the high firing and application temperature, as well.

Constructional design

For the design of the refractory lining, an integrated approach is required, taking into account the reactor geometry, the procedure parameters as well as the characteristics of the ceramic products.

Basic considerations

The walls of the reactors consist of several layers of brickwork. The structure of the layers and the quality selection for the brick backing depend on the design temperature, the desired temperature of the sheet-metal jacket as well as the furnace diameter and the furnace chamber profile. In **figure 4,** the advantages and disadvantages of a two-layer and a four-layer lining are compared

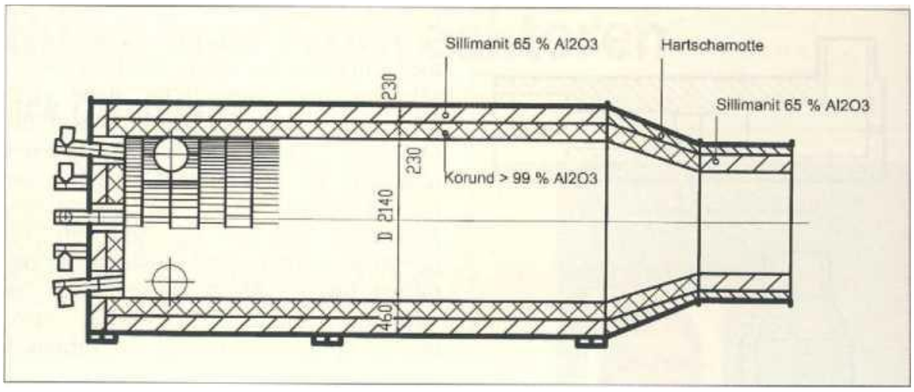

Fig. 5: Refractory lining carcass reactor

by means of heat transition calculations for a carcass reactor. The source data with a design temperature of 1800°C, an internal diameter of 2140mm and a total wall thickness of the lining of 460mm are identical. The theoretical internal surface temperature of the corundum with 1716°C for two layers is 54°C lower than for the four-layer version. The difference with respect to the average brick temperature is even 265°C high. As the chemical reactions between the process gas and the refractory material run faster under higher temperatures, less wear can be expected in case of the two-layer brick lining. However, with a four-layer lining, the temperature of the sheet-metal jacket is significantly reduced from 298°C to 160°C. This results in considerable heat savings due to the lower radiation and convection losses. The refractory materials used are subject to an almost linear thermal expansion when the temperature rises, which is higher than the expansion of the reactor jacket. This causes tensions in the brickwork which close the joints and are therefore desirable.

However, in case of a strong insulation as with the four-layer lining, stress peaks should be prevented by means of appropriate measures such as fine-grained mortar, small brick formats and intermediate layers of refractory paper.

Soft-grade reactor

The refractory lining for this possible type is shown with a horizontal carcass reactor in **figure 5**. In this case, the cylindrical brickwork consists of two layers with standardised arch bricks. The pipes in the front wall for passing through the carbon black oil injection lances are surrounded by shaped brick through the entire depth of the wall. **Figure 6** shows a picture of the inside of the structure after the assembly. For structural reasons, the tangential air and gas nozzles have to be integrated into the cylindrical brickwork with a complex refractory construction. This situation, seen from the inside of the reactor, is shown in **figure 7**.

Hard-grade reactor

The quality of the carbon black mainly depends on the construction of the carbon black generator and the course of the procedure. **Figure 8** shows the refractory

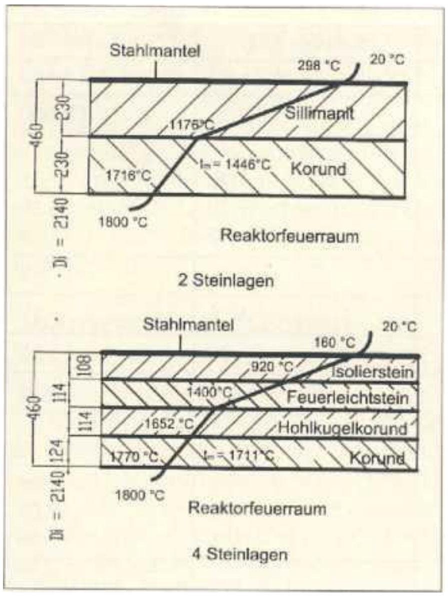

Fig- 4: Heat transition through the reactor wall

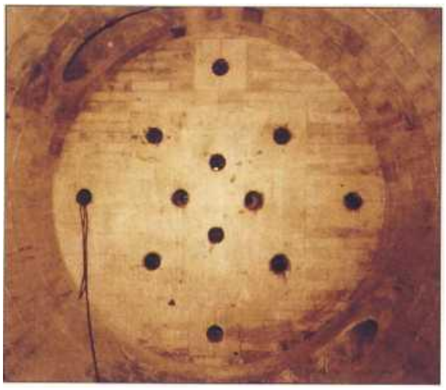

Fig. 6: View on to the front wall

Fig. 7: Entry zone, tangential nozzles

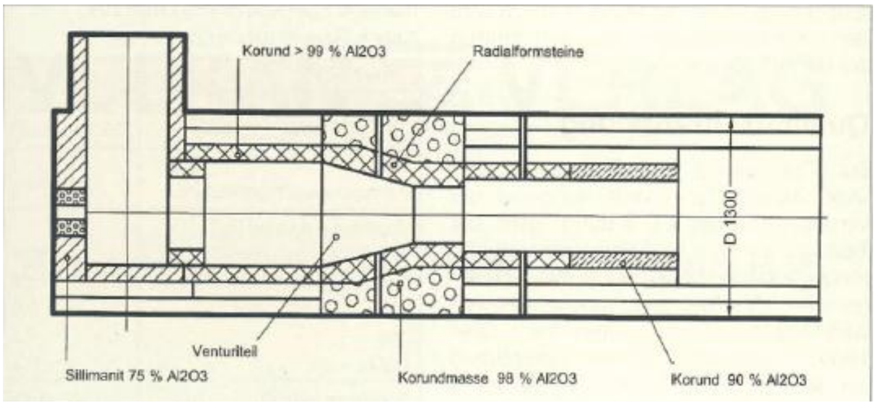

Fig. 8: Refractory lining of the tread reactor

10: Lined reactor components

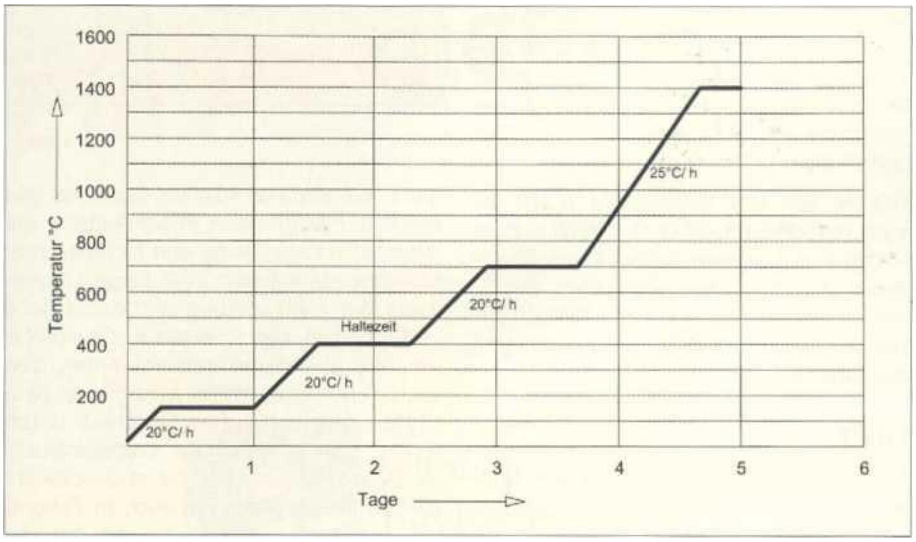

Fig. 9: Heating-up diagram

lining of a tread reactor as a high-performance unit. The main stress occurs in the venturi part up to the water injection. In the conical area, a gas pressure difference is generated due to the increase of the flow rate, which may sometimes result in cross flows between the openings in the brickwork. In the case shown here, the internal lining made of radial shaped bricks is monolithically backed with a refractory mass with high corundum content and an Al_2O_3 content of 98% so that any hot spots can be prevented.

Commissioning

Before production starts, the entire ceramic lining must be dried and pre-heated. By means of a controlled application of heat, any humidity present is slowly extracted from bricks, masses and mortar. The material-specific heating instructions which are drawn up by the supplier must be adapted to the requirements of the furnace commissioning.

Hold points allow for stress equalisation inside the brickwork. Monitoring temperature measurements ensure that the pre-defined drying curve is complied with and local overheating is avoided.

A possible drying and pre-heating diagram is shown in **figure 9**.

Operating experience

When suitable and well-proven refractory qualities are used and the plant is accurately operated, a good durability can be achieved. This does not exclude premature wear of highly stressed parts of the brickwork. This applies in particular to the area between the carbon-black oil nozzle and the water injection. The subdivision of the reactor into individual sections allows for the quick replacement of worn parts. This is especially the case, when the individual reactor components are kept in store readily lined and pre-tempered (**figure 10**). For vertical carbon black generators, a sectional bracing of the brickwork by means of steel brackets is almost impossible because of the high temperatures. A successful ceramic bracing construction is shown in **figure 11**. When the bricks are laid, narrow joints must be formed which must be filled with fine-grained mortar corresponding to the material quality. In the longitudinal direction of the reactor, the expansion of the refractory material under the influence of heat must be taken into account with the realisation of expansion joints.

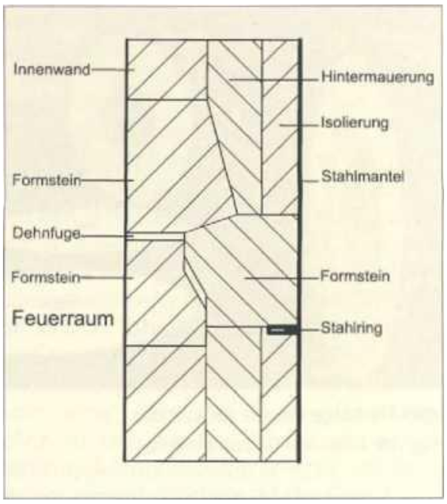

Fig. 11: Ceramic wall bracing

High-temperature fibre paper between the individual brick layers and/or fibre mats around the flanges have proven to be effective. The position and size of the expansion gap must be determined individually. In case of disruptions of operations, it is recommended to maintain the highest possible temperature in the reactors in order to ensure the tension in the lining. If repairs are carried out on the brickwork, possible gaps and cracks should be cleaned but not filled with material in order to avoid excessive compressive stress of the lining. The use of dense and hard shaped bricks with a high corundum content in the inner layer has proven successful in comparison to ramming mixes because of their specific abrasion resistance.

This reduces the grit content, which improves the quality of the carbon black.

Quality development

In order to optimise the quality of the carbon black and the throughput rate and at the same time reduce the generation of CO, there has been a trend to use higher reaction temperatures. For this purpose, it was necessary to develop a refractory material which allows for applications with temperatures of more than 1900°C. Zirconia, for example, has excellent thermal properties. It has a melting point of about 2400°C. However, two modifications of the crystal lattice, which take place subject to temperature following a hysteresis curve, must be reduced to a minimum. These lattice modifications cause the volume of the material to significantly jump up. A small residual effect is however desirable as it improves the resistance to thermal shocks.

We already have first operational results from materials stabilised with calcium oxide (CaO) as well as with yttrium oxide (Y_2O_3) based on the raw materials as indicated above. The property data of a corresponding CaO-doped zirconia brick is shown in **table 4**.

Conclusion

For the refractory lining of carbon-black reactors, there are high-grade refractory brick qualities available for all types of stresses.

Table 4: Property data for Lupudur Z95

Raw material base:	Stabilised zirconia
Max. application temperature [°C]:	2300°C
Chemical analysis [%]: ZrO_2	95.4
CaO	3.8
Al_2O_3	0.2
SiO_2	0.2
Fe_2O_3	0.2
Bulk density [g/cm^{3}j:	4.75
Open porosity [vol.-%]:	16
Compressive strength |MPa]:	50
Thermal conductivity according to the hot-wire method [W/mK] at: 600°C	1.47
1000°C	1.70
1400°C	1.84

The systematic selection of well-proven and successful materials in combination with modern engineering and correct installation guarantee a long service life of the lining and therefore a high availability of the reactors. As a matter of principle, it must however be remembered that even ceramic materials with a very high quality are subject to natural wear and tear. The consequent further development of brick qualities guarantees that the products will still fulfil increasingly demanding requirements for the production of carbon black in the future.