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The Manufacturing of Lightweight Refractories by Direct Freeze Foaming Technique

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ABSTRACT

Refractories are a key component for cost effective and energetic sustainable processes. Depending on the operation temperature of industrial furnace thermal characteristics of porous refractory linings have to be adjusted.
There are a lot of possible porosity adjusting methods, e.g. placeholder, replica and gas injection/development approaches. Now, the freeze-foaming as direct foaming technique shall be introduced as an environmentally friendly way to refractories.
In this presented work an aqueous ceramic mullite suspension is foamed within minutes just by the reduction of the ambient pressure in a freeze drying device. The foam structure suddenly freezes when the suspension temperature, related to the vacuum pressure, reaches the liquid-solid equilibrium line (p,T-diagram of water). The porous structure is then dried by sublimating the frozen water. The resulting bricklike lightweight refractories exhibit a high amount of open porosity and dense struts. Just 5–10 mass-% organic additives, required for a stable foaming, minimize the effect of crack formation during the sintering step and provide an environmentally friendly processing route to the final product.
The pore morphology is being determined by X-ray computed tomographic images and mercury porosimetry. Measurements of the thermal conductivity, compressive strength and creep have been carried out to evaluate the freeze-foaming process as a promising approach for manufacturing refractories.

KEYWORDS

lightweight refractory bricks, ceramic foams, direct foaming, freeze-foaming, X-ray computed tomography, environmentally friendly
Interceram 60 (2011) [6]

1 Introduction

Since the attention of high energy consuming industrial processes is more and more on cost and resource effective ways of operating and environmentally friendly manufacturing, research and development is required to ensure progressive and new promising approaches to reach the requested goals. Arguments for keeping the geometry of kiln and vessels in original shape, reaching reasonable outer temperature for human safety and ultimately controlling the heat loss for a better thermal efficiency and economic operation are to be attended. The ceramic aluminum silicate mullite is well known for its use as refractory material due to its excellent mechanical properties, low coefficients of thermal expansion ($4.5 \cdot 10^{-6} \cdot K^{-1}$) and thermal conductivity as well as high corrosion and creep resistance [1–2]. Many studies have been carried out to improve and optimize its material composition deriving from minerals like andalusite, sillimanite, kyanite [3–5] or its preparation and synthesis from industrial waste like fly ash [6–7] or aluminum-rich sludge [8]. Literature concerning the manufacture of porous material is well known. The main approaches are the REPLICA (burnout of an organic scaffold) and PLACEHOLDER technique (burnout of pore formers like carbon black, sawdust wax and other volatile components) as well as the DIRECT FOAMING (porous structure through gas injection, chemical reaction or mechanical insertion of gas) technique.
Now, this study is introducing a promising alternative approach to create bricklike mullite foam refractories. The so called freeze-foaming comprises the direct foaming of an aqueous suspension and its almost simultaneous freeze drying to a stable ceramic cellular structure. Since typical freeze foamed structures feature dense struts and interconnected pores it is expected to obtain cellular refractories with high compressive strength and required thermal characteristics for their possible use as lightweight linings for kiln and furnace.

2 Experimental

2.1 Processing

The mullite used for this study is the commercially available synthetic sintered Mullite SYMULOX® M 72 (Co. Nabaltec). The chemical composition is that of a stoichiometric mullite ($3Al_2O_3 : 2SiO_2$) consisting of 72 mass-% by Al_2O_3 and 28 mass-% by SiO_2. The chosen powder configurations for this study are the M 72 K0c and K0. Both powders differ in their grain size distribution. The K0c exhibits a d_{50} value of 6.1 µm whereas the coarser K0 has a d_{50}

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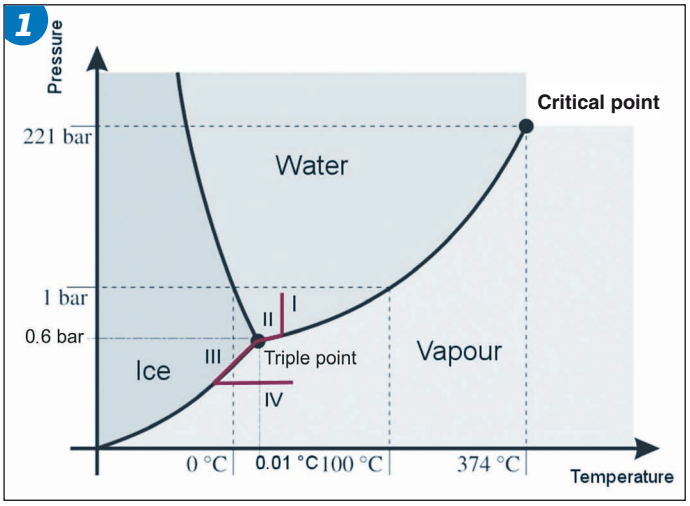

Fig. 1 • p,T-diagram of water (red: process line of the freeze-foaming)

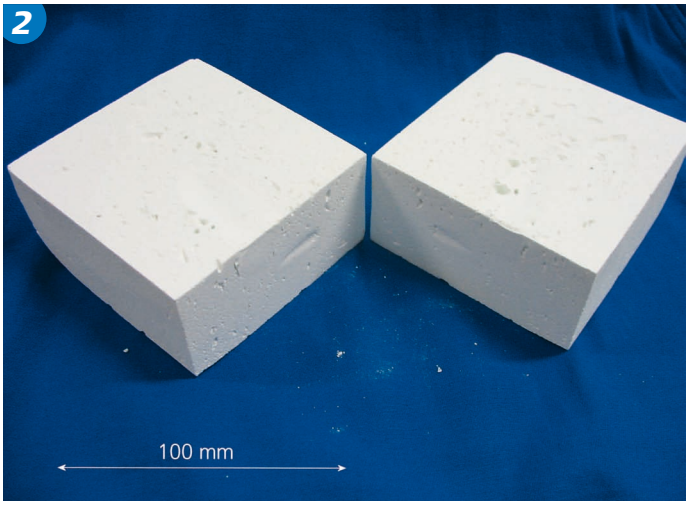

Fig. 2 • Sintered freeze foamed halves of a sintered mullite brick

value of 19.2 µm. To reach a reasonable high bulk density both powders were mixed in a ratio of 40 : 60 (K0c : K0). Experiments were carried out by the means of DoE (Design of Experiments). A fractional factorial 2^{4-1} designed plan was generated resulting in 9 different green (undebinded/un-sintered) mullite foam compositions. As suspension and ultimately foam structure influencing parameters the amount of binder, tenside, solid content and suspension temperature were varied. Thus, after debinding and sintering a different pore morphology as well as different thermo-mechanic characteristics are achieved accordingly.

Now, the obtained foams were prepared in the following way (all amounts related to a 41–52 vol.-% aqueous suspension): 45–52 vol.-% of the mullite powder mixture and 2.5–3.0 vol.-% Methocell (Co. Dow Chemicals, standard grade F4M) were mixed together and treated in a ball mill. After adding 5–7 vol.-% of a PVA-binder (polyvinyl alcohol) and a tenside the whole mixture was then filled into a kneader (K III 5, Co. Linden) and kneaded for 1 h at low rotation. The kneaded ceramic material was then filled into a rubber mould with the inner dimensions of 235 mm × 114 mm × 70 mm. Finally the filled mould is being transferred into the freeze drying device.

2.2 Manufacturing method

The process of the freeze-foaming is based on the decompression of a ceramic or even metallic suspension in the vacuum chamber of a freeze drying device (Co. Christ, Model 1-20). The pressure reduction is leading to inflation. Mainly water vapor but also tiny air bubbles originating from the kneader treatment arise taking the solid matter with them. The former addition of a specific amount of organic binder to the ceramic suspension prevents the bubbles from exiting the progressing foam and leads to a stable foaming condition. Now imagining the p, T-diagram of water (Fig. 1), as the water vapour partial pressure decreases the material system is meeting with the liquid-vapour equilibrium line (Fig. 1, I). Further pressure reduction leads to further foaming and decreasing temperature (Fig. 1, II). Eventually, the system reaches the triple point and the foam freezes immediately (Fig. 1, III). The pressure is being reduced further still and now the panels on which the foamed samples stand are heated. Thus, through sublimation of the frozen water the cellular structure is being dried (Fig. 1, IV). After debinding and sintering a freeze-foamed porous mullite structure is obtained (Fig. 2).

2.3 Characterization methods

In the following studies the most promising mullite structures, originating from the row of specific DoE suspension compositions and further called H06 and H09, are being analyzed. The obtained mullite brick (exemplary sample H09) was characterized due to its macroporous morphology by the X-ray computed tomography (CT Compact, Co. Procon X-ray, X-ray tube max. 150 kV) and the resulting cross section images binarized and analyzed with Image J [9]. Additional information about the mesoporous structure is available with the use of the mercury (Hg)-porosimetry (AutoPore IV, Co. Micrometrics) to DIN ISO 15901-1:2005. For the thermal and mechanical characterization sample H06 was used.

To determine the thermal conductivity the hot wire (cross-array) method (Thermal Conductivity Tester 426, Co. Netzsch) was conducted referring to DIN EN 993-14.

FESEM (Co. Zeiss ULTRA 55) images were taken to visualize the microstructure, particularly struts, pore and grains/grain boundaries. Furthermore, the structural compressive strength was determined at room (INSTRON 8562) and high temperature (MAYTEC) as well as the creep resistance (MAYTEC).

3 Results and discussion

3.1 Pore morphology analysis

The analysis of the binarized CT cross sectional images displayed in Fig. 3 shows a relatively narrow, monomodal pore distribution with a maximum of relative abundance at a pore diameter around 290 µm. The Fig. 4 shows the pore size distribution obtained by Hg-porosimetry. This diagram is roughly bimodal. Corresponding to the bimodal powder mixture the first maximum is reached around 1.5 µm and the second around 30 µm. The small shoulder around 0.02 µm shows the inner porosity of the mullite or the porosity of the struts respectively. In summary it has to be pointed out that the obtained values of both methods reflect only a small volume of the foamed structure. To get information about the volume as a whole more samples do have to be analyzed accordingly. The determined porosities are differing depending on the measurement method. The Hg-porosimetric leads to a porosity of 50.2 % whereas the geometry method (to DIN EN 1094-4) results in 58.2 % with a bulk density of 1.30 g/cm³. However, the geometry method takes the whole brick in-

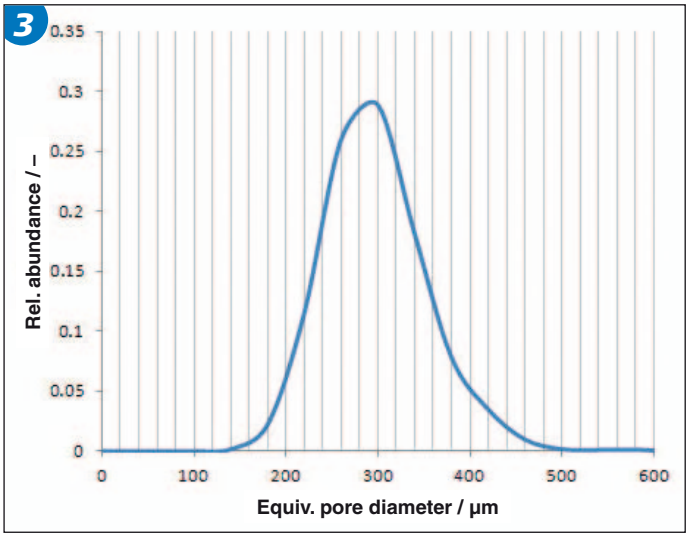

Fig. 3 • Pore size distribution from CT measurements binarized with Image J

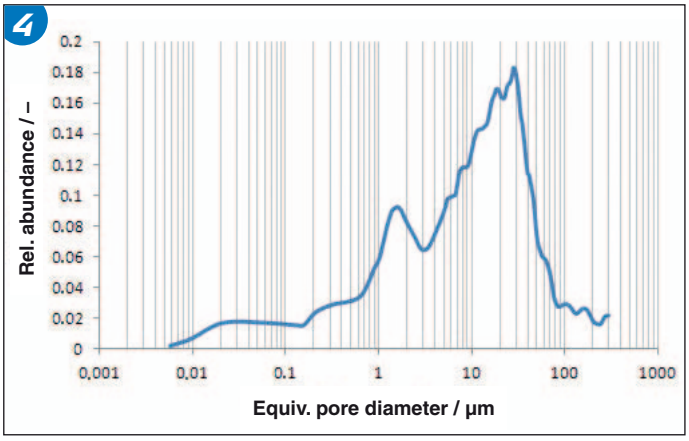

Fig. 4 • Pore size distribution from Hg-porosimetry measurements

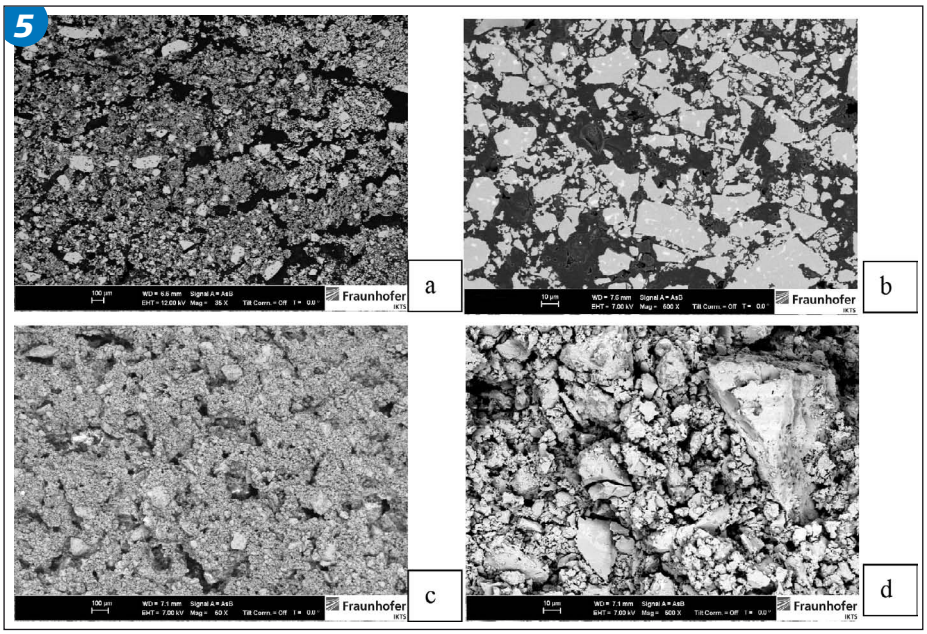

Fig. 5 • SEM images of the obtained mullite brick; a) polished section sample (35×), b) polished section sample (500×), c) fracture surface sample (50×), d) fracture surface sample (500×)

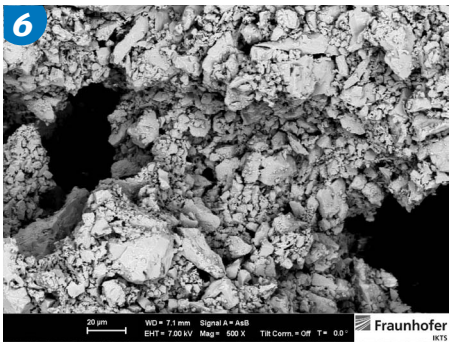

Fig. 6 • SEM close-up images of the microstructure of a porous strut (500×)

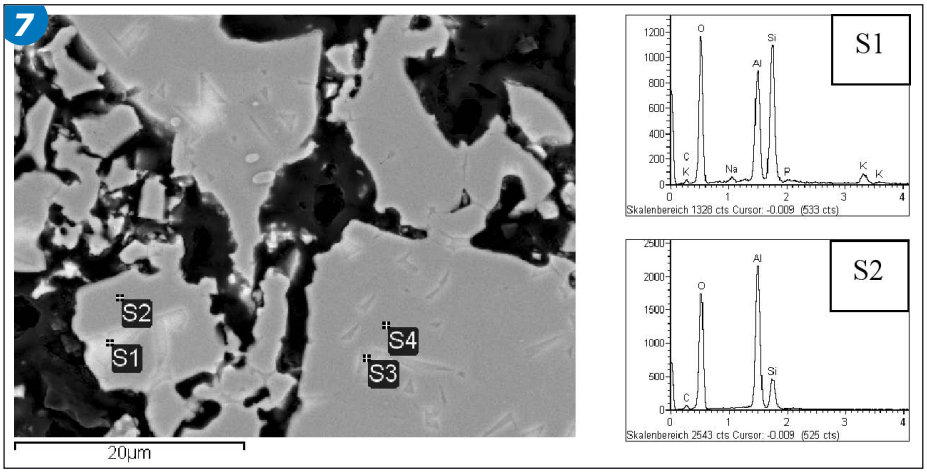

Fig. 7 • EDX measurements of the foamed mullite brick

to account (but possible defects in the structure go missing) whereas the porosimetric data is relying on just a part of the whole volume.

3.2 Microstructure

To obtain information about the microstructure fracture surface and polished section SEM images were taken (Fig. 5 a–d).

In the upper pictures, 5 a–b, the two constituent parts and powders of mullite become apparent. Bigger alumina grains interstratified with silicon enrichments lie in between mostly homogeneous dispersed smaller mullite accumulations in a lose microstructure. This becomes most obvious regarding the images 5 c–d. The Fig. 6 shows the porous microstructure of a strut of the manufactured mullite foam as well as the typical freeze-foamed derived open porosity.

As seen in Fig. 7 the bright appearing enrichments in the bigger mullite accumulations have their origin in a much higher content of silicon.

3.3 Mechanical characterization

For the cold compressive strength (CCS to DIN EN 993-5 and DIN EN ISO 8895) a mullite brick was cut into two halves which were then compressed. The maximum pressure is reached at 39.5 kN/mm² (Fig. 8). With respect to the sample dimensions (114 mm × 100 mm × 50 mm) the CCS adds up to 3.3 MPa.

The high temperature compressive strength mean value (Fig. 9) adds up to 270 N

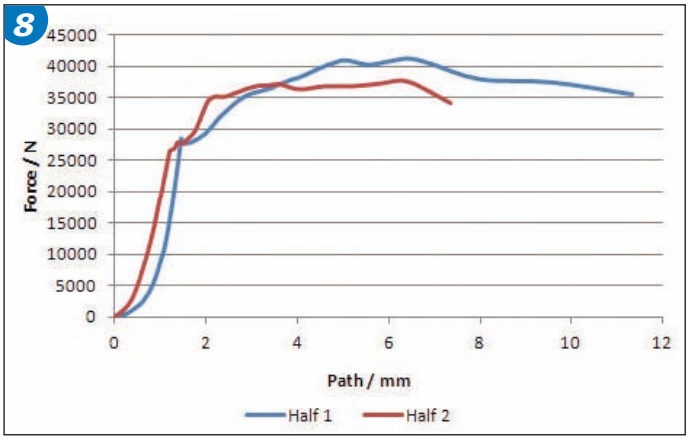

Fig. 8 • Cold compressive strength of two mullite brick halves

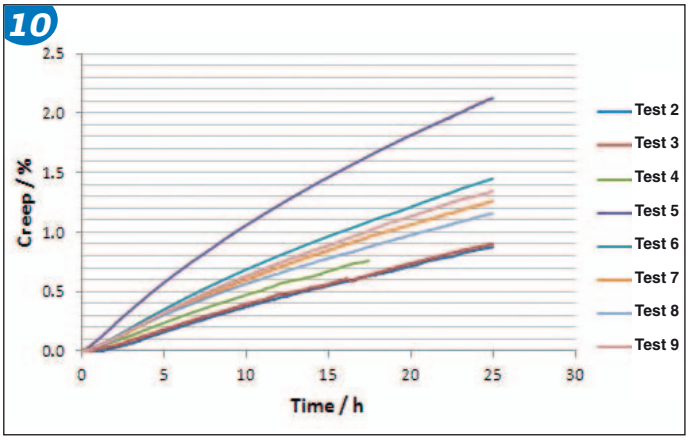

Fig. 10 • Creep resistance of a freeze-foamed mullite brick

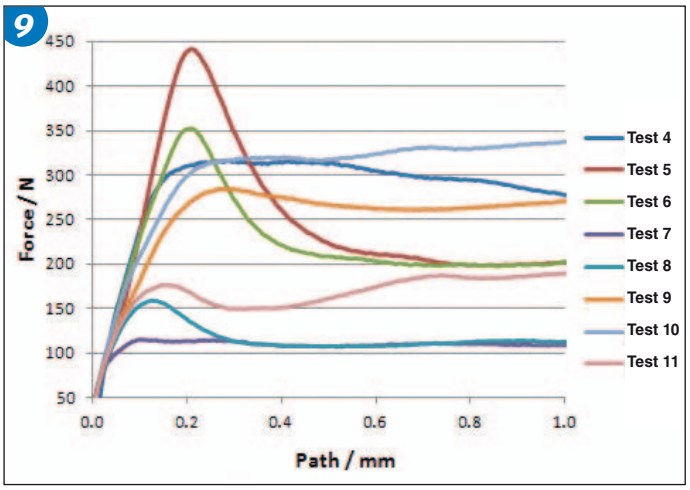

Fig. 9 • High temperature compressive strength of a freeze-foamed mullite brick

(= 0.38 MPa) at 1400 °C referring to DIN EN 993-5 and DIN EN ISO 8895. The maximum strength adds up to 442 N (= 0.6 MPa). However, these values have to regarded critically since the variation of the samples (shape: cylindrical, 30 mm diameter × 50 mm height) is huge. Nevertheless, this variation reflects an apparent inhomogeneity of the porous structure.

Also the creep resistance (to DIN EN 939-9) displays a relatively broad mean variation between 0.9 and 1.45 % (Fig. 10). A somewhat larger defect in the structure is easy to guess regarding the striking graph labeled 'Test 5' and is further treated as an outlier. The mean value of the creep resistance (excluding 'Test 5') of the cylindrical shaped samples (outer diameter 50 mm, inner diameter drill hole 19 mm) adds up to 1.1 % after 1400 °C/25 h under 0.05 MPa loading.

Table 1 • Thermal conductivity of the freeze-foamed mullite bricks

Sample	Thermal conductivity / W/m·K			Bulk density / g/cm³	Porosity / %
	23 °C	400 °C	1200 °C		
H01	0.444	–	0.972	0.99	65
H02	0.535	0.577	0.687	1.38	51
H03	0.505	–	–	1.25	56
H04	0.501	–	–	1.25	55
H05	1.247	–	–	1.25	56
H06	0.300	0.301	0.633	0.78	72
H07	0.746	–	–	1.35	52
H08	0.538	0.454	0.589	1.39	51
H09	0.626	–	0.713	1.29	54

Table 2 • Comparison of the Porrath FL 30-11 [11] and the experimental lightweight brick H06

Sample	Thermal conductivity / W/m·K				Bulk density / g/cm³	Porosity / %	CCS / MPa
	23 °C	400 °C	600 °C	1200 °C			
Porrath FL 30-11	–	0.46	0.46	0.53	1.1	65	5
H06	0.300	0.301	–	0.633	0.78	72	3.3

3.4 Thermal conductivity

For all according to the DoE manufactured foams the thermal conductivity was measured (Tab. 1). Due to its low thermal conductivity coefficient, especially the mullite brick H06 is a promising candidate as lining for kiln and furnace. In general, the variation of the resulting coefficients is an image of the different suspension compositions in the beginning of the process and according to the DoE plan. Around a porosity between 51 and 56 %, the thermal conductivity of the four different foams H02, 3, 4 and H08 is very similar at a temperature of 400 °C. Reflected to the similar bulk density the pore size seems to be very much alike.

3.5 Discussion

In Table 2, specifications such as the thermal conductivity, bulk density, CCS and porosity of the freeze-foamed mullite brick H06, are compared to the "state of the art" lightweight refractory brick Porrath FL 30-11 (composition: 74 mass-% Al_2O_3, 25 mass-% SiO_2, 0.3 mass-% Fe_2O_3) of the Co. Rath. Regarding the thermal conductivity the manufactured foams are fitting the proposed diagram (Fig. 11) very well and can be classified as lightweight refractory bricks. In comparison to the Porrath FL-30-11 the freeze-foamed sample H06 has a lower coefficient at lower temperatures but a higher coefficient at high temperatures. Considering the pore size, the higher the temperature the higher the heat radiation is coming to the fore. Thus, according to the foams high porosity of 72 % (to 65 % of the FL30-11)

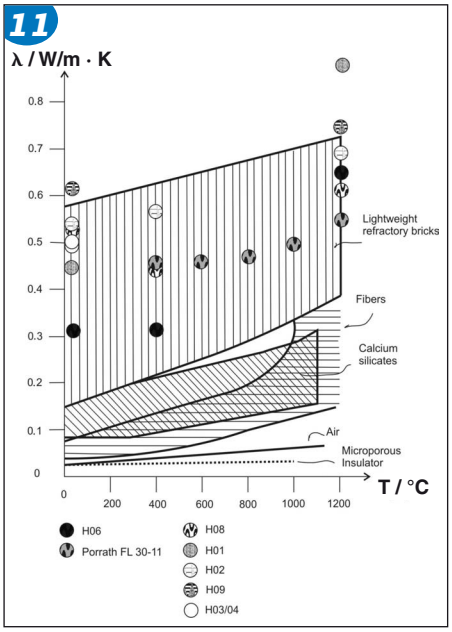

Fig. 11 • Thermal conductivity vs. temperature of refractories [10], comparison with the freeze-foamed mullite bricks and the "state of the art" lightweight brick Porrath FL 30-11

and low bulk density of 0.78 g/cm³ (to 1.1 g/cm³ of the FL 30-11) the thermal conductivity coefficient is increasing. So, the as to-be state regarding a successful mass product, requires a pore size decrease and bulk density increase to reach reasonable thermal conductivity values for high temperature applications. However, for a medium temperature range up to 400 °C the manufactured lightweight refractory brick marked H06 is very promising.

4 Conclusion and future prospects

This study shows that it is possible to create and manufacture new porous lightweight bricks made of mullite by applying the freeze-foaming technique. With further research concerning the material composition, adjustment of the optimal pore size and increasing bulk density freeze-foamed refractory bricks seem very much within reach to usual state of the art products. However, the experimental setup is still in laboratory scale and needs up-scaling to be fully comparable to lightweight refractory mass production. Regarding small batched products of a more complex design the freeze-foaming might be successful already.

Acknowledgement

The author wants to thank the Fraunhofer Society for the financial support as well as the company RATH for supplying the quality control data of the Porrath FL 30-11. Also lots of thanks to the Freiberger IKGB for the thermal conductivity measurements.

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Received: 07.09.2011