IMPROVING PROPERTIES OF MAGNESIA-SPINEL BRICKS FOR CEMENT ROTARY KILNS BY USING MICRO-FINE MgO PARTICLES

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ABSTRACT

Micro-fine MgO particles were added to a standard magnesia-spinel refractory brick formulation with the aim to improve the physical properties of the fired bricks. The addition of micronized MgO particles lead to a higher bulk density, higher cold crushing strength, lower apparent porosity and lower gas permeability compared to reference magnesia-spinel bricks. Moreover, the hot physical properties refractoriness-under-load, creep-in-compression as well as the cold and hot modulus of rupture were enhanced. A field trial was carried out in a cement plant to assess the performance of the improved bricks in service.

Keywords: particle size distribution; cement rotary kiln; magnesia-spinel bricks

INTRODUCTION

The fine fraction of particles or the so-called matrix plays an important role for the physical properties of refractory bricks[1]. It is obvious that the pore space related parameters porosity and permeability are directly related to the distribution of the fine fraction throughout the brick volume. Furthermore, the density of refractory bricks can be increased by filling the pore space with fine particles. Due to their high specific surface area and the large amount of contact points, fine particles have the tendency to sinter at lower temperatures compared to larger ones. Therefore the crushing strength of refractory bricks can be significantly improved by a well distributed fine fraction. Theoretically, the void space in a porous medium could be filled almost completely if the particle size distribution followed a fractal model which means that a sufficiently small particle fits into every void between at least three particles. In reality the introduction of fine particles into the pore space is limited to a certain lower threshold for the particle size which is determined by the tendency of fine particles to agglomerate and by the existing production methods of fine particles (e.g. ball mills). Packing theories are widely applied in refractory engineering as well as in other applications like the development of high performance concretes[2]. A practical example is the use of the Andreasen model[3] or a modified Andreasen model for the development of dense refractory castables and bricks[4]. A continuous trend towards a larger amount of particles < 100 µm can be observed over the last decades in magnesia-spinel refractory brick formulations.

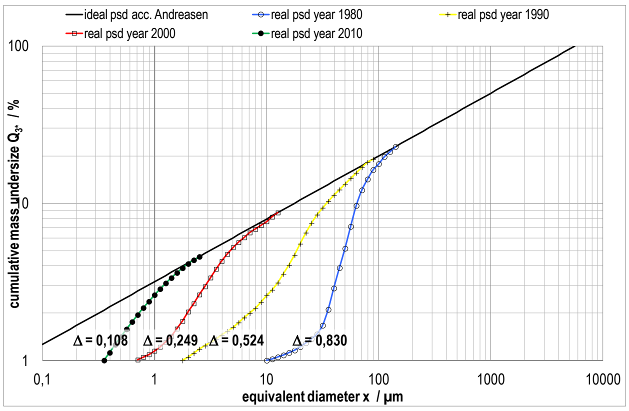

Fig. 1: Development of particle size distributions (PSD) in the fine fractions of basic refractory bricks from 1980 to 2010.

The deviation of the real particle size distribution (PSD) from an ideal PSD, expressed as delta, is shown in Figure 1. Over the last decades the real PSD approached much closer to the PSD of an Andreasen model and the delta area between the ideal and the real PSD came down from 0.83 to 0.11. As a result denser refractory bricks with less apparent porosity were achieved. Recently the use of nano-sized particles has increased in many refractory related ceramic applications with the aim to fill even the void space between the micrometer-sized particles[5].

In the present study micro-fine MgO particles were added to magnesia-spinel brick formulations. The aim was, besides reducing the porosity and permeability, to improve the sintering behaviour during firing. Moreover, it was also intended to promote the in-situ spinel formation via the reaction of dispersed MgO with Al_2O_3 in the pore space.

MATERIALS AND METHODS

Micro-fine MgO particles were produced from very pure Brazilian magnesia sinter after ballmilling with an MgO share of typically > 98 %. The generated micro-fine particles had a diameter from 0.5 to 4 µm with a median-diameter (d_{50}) of 1.6 µm as determined by laser diffraction. The micro-fine MgO particles were prepared as an oil-based slurry with a solid content of 75 %. The change of the PSD during the preparation of the micro-fine MgO particles is shown in Figure 2.

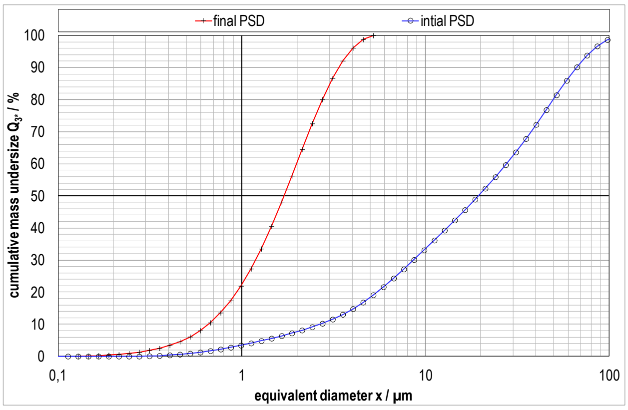

Fig. 2: Change of the PSD during preparation of the micro-fine MgO particles. The PSD of the initial BMF material and of the final micronized product are shown.

Chemical analysis of the initial ball mill fines MgO (BMF) and of the generated finished product was measured by XRF on fused beads in accordance with DIN EN ISO 12677:2013 (Table 1). The Loss on Ignition (LoI) was determined by the mass loss during fused beads preparation. No remarkable change in chemistry was observed due to the comminution process. The micro-fine MgO particles were added to a standard magnesia-spinel formulation during mixing.

In a first step series of test cylinders were produced in laboratory scale to optimise the necessary quantity of micronized particles in order to achieve the lowest possible porosity and the best packing density, respectively. Based on the successful laboratory results it was decided to produce an amount of approx. 2.5 tonnes micro-fine MgO slurry for an industrial scale production of a new brick type.

In this trial production a lot of approx. 50 tonnes rotary cement kiln liners were manufactured in the brick plant, applying the normal production route but adding the micro-fine MgO slurry into the mixing process. For comparison a lot of standard magnesia-spinel bricks without micronized particles were also manufactured.

From both lots green bricks were sampled directly after pressing. Also, a sufficient number of samples were collected after firing the bricks in a high temperature tunnel kiln. All sampled bricks were tested with respect to their standard physical properties: bulk density, apparent porosity, gas permeability and cold crushing strength (CCS).

Tab. 1: Chemical analyses and particle sizes of the initial MgO BMF and the manufactured micronized MgO particles.

	Unit	MgO initial BMF	micronized MgO particle slurry
Chemical analyses			
CaO	mass%	0.89	0.95
MgO		98.21	97.90
SiO_2		0.33	0.32
Fe_2O_3		0.36	0.55
Al_2O_3		0.11	0.15
Mn_2O_3		0.09	0.10
Cr_2O_3		0	0
TiO_2		0.01	0.03
P_2O_5		0	0
ZrO_2		0	0
Particle size distribution			
d_{10}	µm	2.7	0.7
d_{50}		19.5	1.6
d_{90}		66.5	3.4

Furthermore, the important hot properties like refractoriness-under-load (RuL) up to 1700°C and creep-in-compression (CiC) at 1500°C were determined on cylinder subsamples. The cold and hot modulus of rupture (CMoR / HMoR) of the finished products were tested in accordance with DIN EN 993-7 at 20, 1200, 1300, 1400 and 1500°C. The stress and strain applied on the test pieces was simultaneously recorded during the CMoR and HMoR tests.

For proving the suitability of the new brick type the new bricks were installed for a field trial in a 2.8 m section of the lower burning zone of a 4.8 m diameter cement rotary kiln. The standard magnesia-spinel reference bricks were installed directly adjacent to the trial bricks to assess the performance of the trial bricks compared to the reference bricks.

RESULTS

The chemical compositions of samples of the standard bricks (reference) are shown in comparison to the trial bricks with the addition of micro-fine MgO particles (Table 2). The data show that the MgO content was increased whereas the Al_2O_3 content was reduced by approximately the same amount due the addition of the micro-fine MgO particles. The concentrations of the other constituents were similar in both formulations.

Tab. 2: Chemical composition of the magnesia-spinel reference bricks and the trial bricks with addition of micro-fine MgO particles.

	Unit	magnesia-spinel reference bricks	magnesia-spinel trial bricks
Chemical analyses			
CaO	mass%	0.72	0.72
MgO		87.95	88.63
SiO_2		0.30	0.31
Fe_2O_3		0.37	0.37
Al_2O_3		10.57	9.87
Mn_3O_4		0.07	0.08
Cr_2O_3		0	0
TiO_2		0.01	0.01
P_2O_5		0.01	0.01
ZrO_2		0	0

Comparison of the standard physical properties and the CMoR of the trial bricks with the magnesia-spinel reference bricks reveals that these properties were significantly improved (Table 3). The fired bulk density of the bricks increased significantly by 0.05 g/cm³; the apparent porosity decreased by 1.3 vol.% absolute. This trend was accompanied by a decrease in gas permeability of about 0.2 µm² and an increase in CCS of 5 MPa. The CMoR measurement yielded a relative increase of about 25% for the trial bricks compared to the reference bricks. This increase in CMoR was accompanied by a 10% higher maximum strain.

Tab. 3: Comparison of different physical key properties of the magnesia-spinel reference bricks to the trial bricks with the addition of micro-fine MgO particles.

	Unit	magnesia-spinel reference bricks	magnesia-spinel trial bricks
Physical properties at room temperature			
bulk density	g/cm³	2.916	2.974
apparent porosity	vol.%	15.9	14.6
gas permeability	µm²	0.79	0.48
CCS	MPa	61	66
CMoR	MPa	4.2	5.6
max. strain	‰	1.8	2.0

The analysis of the hot properties indicates that the mechanical behaviour of the refractory bricks at temperatures up to 1700°C was further improved by the addition of micro-fine MgO particles (Table 4).

Tab. 4: Comparison of RuL, CiC and HMoR of the magnesia-spinel reference bricks to the trial bricks with the addition of micro-fine MgO particles.

	Unit	magnesia-spinel reference bricks	magnesia-spinel trial bricks
Refractoriness-under-Load @ 300 K^{-1} and 0.2 MPa			
T_{05}	°C	> 1700	> 1700
Creep-in-Compression @ 1500°C and 0.2 MPa			
Z_{10}	%	0.58	0.48
Z_{25}		0.99	0.84
Hot modulus-of-rupture			
@ 1200°C	MPa	5.6	10.0
@ 1300°C		3.9	7.2
@ 1400°C		1.9	3.9
@ 1500°C		1.6	2.4
Hot maximum strain			
@ 1200°C	‰	3.1	4.6
@ 1300°C		4.0	4.5
@ 1400°C		3.2	5.1
@ 1500°C		2.4	3.6

The refractoriness-under-load T_{05} showed figures of > 1700°C for the reference brick samples and for the trial brick samples. The creep-in-compression test revealed that the reference brick samples and the trial brick samples deformed only slightly but an improvement by the addition of micronized MgO is visible.

The HMoR was measured in 100 K intervals from 1200°C to 1500°C and showed significantly higher values for the trial brick samples in comparison to the reference bricks. The simultaneously recorded maximum strain indicate that the trial bricks can absorb approx. 50% more strain than the conventional bricks before collapsing.

DISCUSSION

The data shown in the previous section indicate that the physical properties of the trial bricks were improved significantly compared to the reference bricks. The addition of micro-fine MgO particles to a conventional magnesia-spinel brick formulation obviously lead to a better packing of the brick matrix which positively influenced the fired bulk density, the CCS, the porosity and the permeability. It must be noted that the densification of the brick matrix did not lead to a higher brittleness at room temperature but rather to a material that could absorb higher strain before final destruction as documented by the higher CMoR and maximum strain values at 20°C (Table 3).

The creep-in-compression at 1500°C and the HMoR measurements from 1200 up to 1500°C indicate that the denser brick matrix lead to a higher resistance against mechanical deformation at high temperatures (Table 4). The HMoR values showed a relative increase of 80% in average compared to the reference. The addition of the micro-fine MgO particles yielded HMoR results comparable to typical values of superior-grade magnesia-spinel-zirconia bricks (Figure 3). These magnesia-spinel-zirconia bricks are specifically designed to present a high HMoR in particular at very high temperatures when a cement rotary kiln is overheated.

The fact that the trial bricks reached similar HMoR results as typical magnesia-spinel-zirconia bricks indicates clearly the positive impact of the micro-fine magnesia addition on the microstructure of the bricks and can be explained by an improved sintering resulting in a much higher number and much stronger contact points between the larger grains per unit volume. Such a texture reduces the probability of fatal crack propagation.

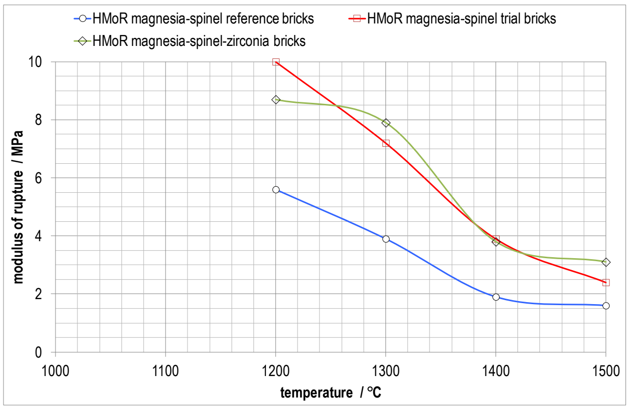

Fig. 3: Comparison of HMoR values of the trial bricks with the reference and with superior-grade magnesia-spinel-zirconia bricks.

The maximum strain in the HMoR measurement is a measure to describe the flexibility of a material. The maximum strain of the trial bricks was increased relatively by 70% compared to the reference (Table 4). The combination of lower porosity and permeability with higher density, higher CCS, lower creep-in-compression and improved HMoR and flexibility indicates that the performance of these refractory bricks in service should improve. Thus, the trial bricks might be potential candidates to be installed in mechanically challenging areas in cement rotary kilns like, e.g. in the tyre area.

To prove this hypothesis it is intended to sample the trial and reference bricks from the test installation in the 4.8 m diameter cement rotary kiln after a one year campaign and carry out an extended post-mortem investigation possibly showing the potential failure mechanisms and the infiltration mechanisms. Upon the closing date for the paper submission the campaign in the cement plant is still ongoing; the novel trial bricks are now 12 months in service. Thus the investigation results of this field trial will be subject of a further study.

CONCLUSIONS

The current study shows that it was possible to improve the physical properties of magnesia-spinel refractory bricks by the addition of micronized MgO particles. These particles fill the void space between the larger grains and promote the sintering of the larger grains as well as the in-situ spinel formation in the pore space. It could be shown that the micro-fine MgO particles not only improved the densification of the brick matrix but also lead to a higher flexibility of the bricks. The technology has been up-scaled from the laboratory scale to a real industrial scale and the trial bricks were successfully installed in a cement rotary kiln. From all figures tested it can be derived that the brick performance should increase. However, this prediction is still in verification.

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