MONOLITHIC REFRACTORIES DESIGN WITH IMPROVED STRENGTH DUE TO SMART PARTICLE DISTRIBUTION IN SIZE AND SHAPE

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ABSTRACT

Particle interlocking plays the most important role in the formation of physical and mechanical properties and is dependent on optimized particle distribution in size and shape composing in the refractory monolithic formulation. The aim of the project is to define a procedure that allows individual adjustments for the grain size distribution with special consideration to the aspect ratio of the grain size, that are analysed with computerized particle analysis (CPA).

In this early project stage, tabular alumina and fused mullite were investigated in terms of adjustment to the best possible packing and interlocking of particles. The optimization process was investigated by means of working properties e.g. mixing properties by measuring the energy input, water demand, rheology, densification, drying shrinkage and green strength.

The detailed and quantified results of this optimization process provided a much deeper understanding of how the particle size, shape and surface roughness influence the working properties of refractory monolithics and therefore provide comprehensive information about improved particle size distribution.

The systematically correlation of the particles' nature with the optimized grain size distributions result in optimized workability to obtain refractory monolithics with the best possible physical and mechanical properties.

Furthermore, the results of this project will enable flexible response of refractory producers to changes in particle shape of raw materials, which already ran through a process (recyclate).

INTRODUCTION

Today the refractory industry is facing the challenging situation that the availability of highly defined raw materials decrement incessantly due to limited raw material resources and an increasing demand of the local industry that provide important raw materials as e.g. refractory grade bauxite. Furthermore, European legislation identified the entire ceramic industry as a resource demanding industry that has a high potential to safe raw materials in terms of the use of a higher percentage of recycled raw materials. Significant innovation and development potential, regarding efficiency-, substitution- and recycling measures, within the whole value-added chain, are perceived. It can be expected, that constitutionally measures, focused on the use of secondary resources, for manufacturing companies to reach the "Best Available Techniques Reference" (BREF), lie ahead.

Particularly for the refractory industry recycling poses a challenge because raw materials change their nature in chemical and mineralogical composition. Especially the interaction with processed materials that are in liquid or gaseous conditions affects the refractory material. Proper separation of infiltrated (affected) materials from solely thermally loaded material is indispensable. The recyclate must be carefully chemically and mineralogically inspected. Especially the glass content changes the technological properties significantly. With increasing (first) lifetime the glass content can increase significantly.

In further the thermal load during the first life of refractory raw materials influences the material properties like grain size, shape, their surface character and typically their open porosity.

While the chemical and mineralogical properties can be easily checked the nature of grains in terms of shape and their surface character can be various. This is of special importance because after the first use the breakout material consists of rigid ceramic bond blocks that are characterized by a distinct primary grain size distribution before it can be used as a recyclate. It must be crushed and classified into specific grain fractions. The nature of grains depends on the raw material itself and the temperature load during the first lifecycle. The latter affects the bonding strength between the particles.

Below the line, refractory producer will face a larger variety of raw materials in terms of their technological specification. It is of common knowledge that the aspect ratio of the grains strongly affects the production process of dense refractory materials. This appears be more challenging for refractory castables. For good installation properties, it will be necessary to adjust the grain size distribution, the water demand and the nature of dispersant dynamically within an ongoing production process. Soon quality management processes may have to include more dynamic possibilities to adjust recipes as a countermeasure to provide refractory materials with technological properties that are accepted by the user industry. For the implementation in a quality management the changes in the recipes must be systematic and traceable.

However, no specific procedures to quantify the influence of particle morphology on the packing behaviour described in the literature. There are various packing algorithms, developed for and limited to spheres, spheres composites or analytical shapes like ellipses, ellipsoids, spheroids and cylinders to this day. When talking about accomplishing a packing algorithm for arbitrary shapes, the difficulty of mathematic modelling of non-spherical shaped particles plays an essential role [1-4].

Approaches for the usage of grain images to analyse the particle packing-behaviour are already described in the literature: X. Jia et al. [4, 5] concentrated on packing of arbitrary shapes and developed a packing algorithm for particles with complex shapes. This packing algorithm deals with the digitisation of drawn or scanned images of real particle shapes and a variable packing space in terms of pixels in 2D or voxels in 3D. The usage of this algorithm shall enable the prediction of packing characteristics of particles of arbitrary shapes.

As this algorithm was not evaluated for refractory monolithics up to now, there is no information about the practical value. But the idea of using grain images to generate the best possible particle packing of refractory monolithics shows a high potential for a dynamic adjustment of the grain size distribution that is independent from the particle shape. This will deliver a high flexibility in the production process of refractory monolithics, because independently on the grain characteristic the grain size distribution can be adjusted by solely measuring the grain shape.

This paper informs about preliminary results how the nature of grains can be implemented in a systematic adjustment of particle size distribution to overcome problems that will arise with increasing quantities of secondary raw materials in refractory castables.

ANALYTICAL METHODS

Particle size and shape analysis

A computerized particle analysis (CPA) device (type 2-1, HAVER & BOECKER) was used for the investigation of size and shape of the coarse grain fractions (from 0.2 to 6 mm) according to table 1. The HAVER measurement method is based on digital image processing for dynamic image analysis of dry, non-agglomerating bulk solids [6].

The particle morphology of tabular alumina and fused mullite coarse grains (Fig. 3) were analysed and compared for here reported preliminary investigations. In the first attempt these investigations were conducted to get an idea how differences in grain morphology will be digitised by the CPA software.

Table 1. Recipes of the reference castable and three preliminary mixtures where coarse grain tabular alumina fractions were substituted by fused mullite

Component	**Weight-%**			
	REF	FM1	FM2	FM3
Tabular alumina				
3-6 mm	16	16	16	16
1-3 mm	21	-	-	21
0.5-1 mm	11	-	11	-
0.2-0.6 mm	10	10	10	10
0 – 0.2 mm	11	11	11	11
0 – 0.045 mm	9	9	9	9
Fused mullite				
1.6-3.2 mm	-	21	21	-
0.7-1.6 mm	-	11	-	11
Calcined alumina	10	10	10	10
Reactive alumina	7	7	7	7
CA cement (70 wt.-% Al_2O_3)	5	5	5	5
Sum	**100**	**100**	**100**	**100**
Water	4.4	4.4	4.4	4.4
Dispersing agent (PCE)	0.15	0.15	0.15	0.15

The CPA device was also used to measure the particle size distribution of the grains with sizes ≥ 200 µm. Due to insufficient pourability, leading to agglomeration of the particles, components ≤ 200 µm could not be investigated with the CPA device in a sufficient precision. Depending on the grain sizes of the investigated fraction 25 to 250 g of the raw materials were used. The CPA software provides the possibility to choose variable sieve graduations to compare the PSD testing results with any existing sieve analysis. For these investigations the sieve graduation was chosen according to ISO 1927-3.

To describe differences in the particle shape of the coarse grain fractions TA 1-3 mm, FM 1.6-3.2 mm, TA 0.5-1 mm and FM 0.7-1.6 mm., circularity and aspect ratio, l/w are plotted against the cumulative volume (fig. 4 and 5). The circularity is defined as the circumference of a projection-coextensive circle with regard toward the true projection surface (Eq. 1).

$$\Psi_z = \frac{2 * \sqrt{\pi * A1}}{U_p} \qquad \text{(Eq. 1)}$$

where, Ψ_z is the circularity, U_p is the measured circumference of the projection surface and A1 is the measured projection surface [9].

Castable Preparation

Four different self-flowing refractory castables according to table 1 were investigated within the preliminary testing. As reference mixture (REF) a cement bonded 3-6 mm high tabular alumina castable was chosen. Three other batches were created by substituting the coarse grain fractions 1-3 mm and/or 0.5-1 mm by 1.6 - 3.2 mm and/or 0.7 – 1.6 mm fused mullite.

Fig. 1 shows the particle size distributions in terms of cumulative percent finer than D (CPFT) of each investigated refractory castable mixture (tab. 1). The grains with sizes ≥ 200 µm were measured by CPA device and the values for grains with sizes ≤ 200 µm were measured by laser granulometry. The curves show no significant differences and are comparable with distribution modulus q of 0.16 acc. to Dinger and Funk's *Alfreds's packing model* [8].

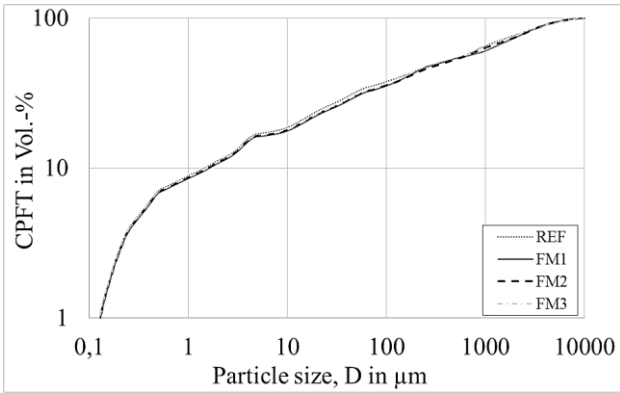

Fig. 1: CPFT in Vol.-% against particle size, D curves of one cement-bonded self-flowing high alumina castables (REF) and three self-flowing high alumina castables with grain fraction substitutions by fused mullite (FM1, FM2 and FM3).

To ensure a proper mixing, an intensive mixer (type R02, EIRICH) was used with a stick agitator and concurrent rotation for mixtures ≤ 4 kg and star agitator and contrarious rotation for mixtures ≥ 4 kg, 700 rpm applying 1 min dry mixing and 5 min wet mixing. Fig. 2 shows the mixing power against the mixing-time, which is quite similar for all four mixes. Homogenisation proceeds rapidly within a view seconds at the beginning of dry mixing. Afterwards the mixing power stays on a constant level. The mixing power increases up to its maximum within approx. 30 seconds, caused by the addition of water after 1 min into the dry mixtures. The formation of agglomerates transit to plastically behaviour. After a short plateau the mixing power decreases slowly during the homogenizing process till constant energy input after 5.5 min. This means the mixing quality reached its maximum homogenisation and the agglomerates are fully disintegrated. Consequently, the mixtures should show ideal working properties and material characteristics.

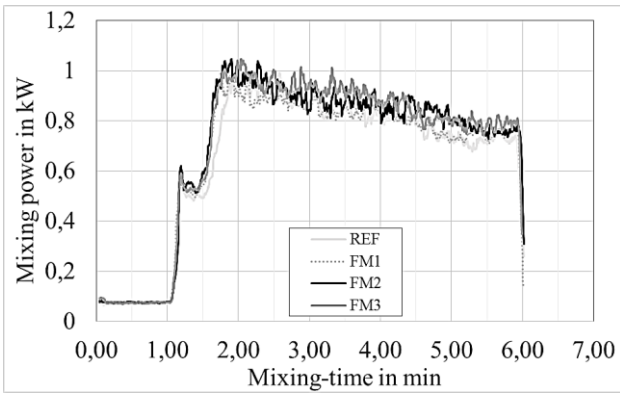

Fig. 2. Mixing power in kW against mixing-time of one cement-bonded self-flowing high alumina castables (REF) and three self-flowing high alumina castables with grain fraction substitutions by fused mullite (FM1, FM2 and FM3).

All samples were moulded in format “D” shapes (160x40x40 mm) according to ISO 1927-5. After 24 hours, the samples were demoulded and cured for further 24 hours whereby over the entire procedure the curing conditions (temperature and relative humidity) were kept constant at 20 °C and relative humidity of 95 % in a climate cabinet. Thereafter the samples were dried to constant mass at 100 °C in a heating cabinet and were immediately tested after 24 hours of soaking time.

Analysis of working properties and technological characterisation

The rheological properties of the resulting self-flowing castables were analysed by applying the slump flow test. This test was investigated time resolved by using digital photo records during the traditional slump flow test setup on basis of ISO 1927-4 as reported by L. Klein and O. Krause [7].

Within 2 minutes after the mixing time, the slump flow measurement was started to ensure a similar initial situation for all samples.

Furthermore, the influence on the cold modulus of rupture and bulk density/open porosity after drying was analysed according to ISO 1927-6.

RESULTS AND DISCUSSION

Particle characterisation

The raw materials were characterised concerning their particle size distribution and their morphological appearance. Fig. 3 envisages their occurrence under the microscope. As typical for tabular alumina the surface appears rough due to their nature of production as a sintered raw material (fig. 3 (a) and (c)). On the contrary fused mullite is shaped by smooth fracture surfaces that relate to the crystal structure of a single crystal mullite. On the first glance, tabular alumina appears splinterier than mullite that typically occurs as prismatic more isometric shapes.

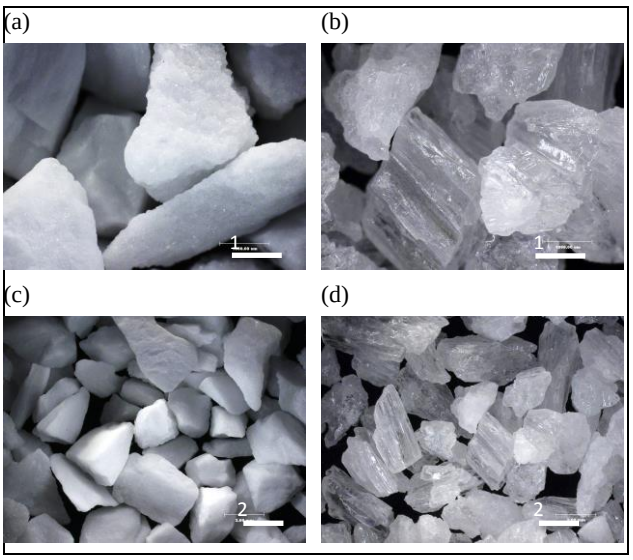

Fig. 3: Particle morphologies of refractory raw materials: (a) and (c) 1-3 mm tabular alumina, (b) and (d) 1.6-3.2 mm fused mullite, Digital microscope VHX-500F, KEYENCE.

The grain fractions were also measured with the CPA device and are summarized in fig. 4 and 5. Fig. 4 shows that the average circularity for TA 1-3 mm, FM 1.6-3.2 mm and FM 0.7-1.6 mm is with 0.83 similar. For TA 0.5-1 mm a slightly higher value of 0.84 was measured. TA 0.5-1 mm appears to be the fraction that is more isometric than the other fractions.

The distributions of aspect ratio, l/w, of the said fractions as plotted in fig. 5 show with 1.5 a higher average aspect ratio for TA 1-3 mm that is higher than for FM 1.6-3.2 mm, FM 0.7-1.6 mm and TA 0.5-1 mm that lie at an identical value of 1.4.

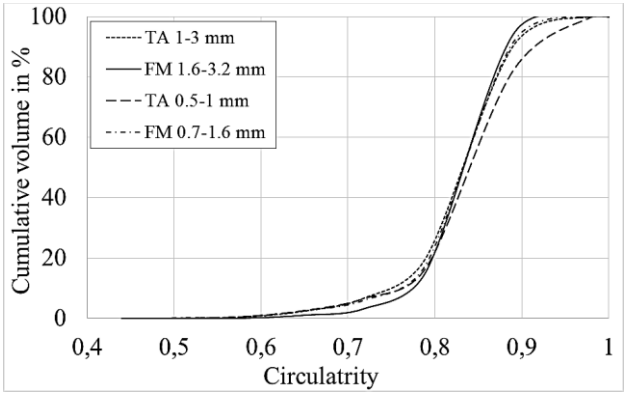

Fig. 4: Cumulative volume against circularity of tabular alumina (TA) 1-3 mm and 0.5-1 mm and fused mullite (FM) 1.6-3.2 mm and 0.7-1.6 mm, measured with CPA device type 2-1, HAVER & BOECKER.

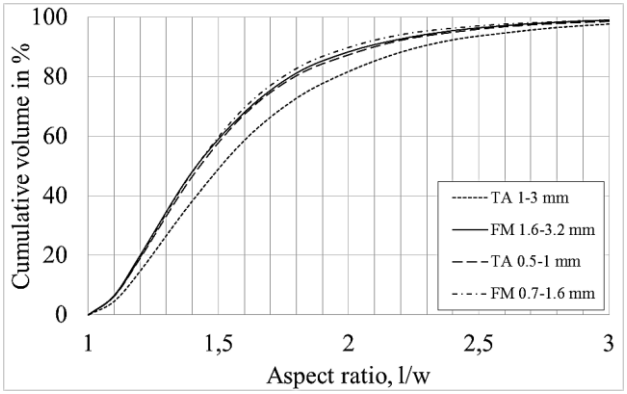

Fig. 5: Cumulative volume against aspect ratio, l/w of tabular alumina (TA) 1-3 mm and 0.5-1 mm and fused mullite (FM) 1.6-3.2 mm and 0.7-1.6 mm, measured with CPA device type 2-1, HAVER & BOECKER.

Influence of the particle characteristics on the workability

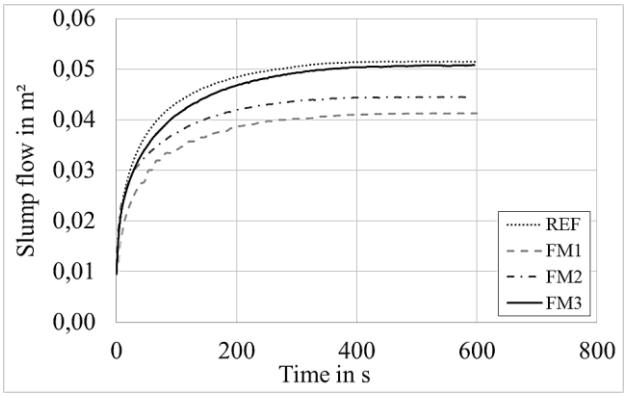

Figure 6. Slump flow area in m^2 against time of one cement-bonded self-flowing high alumina castables (REF) and three self-flowing high alumina castables with grain fraction substitutions by fused mullite (FM1, FM2 and FM3).

Fig. 6 shows the results of the slump flow test of the four mixtures. The final spread and stoppage time of mixtures REF and FM3 are very similar. With values of 0.052 m² / 0.051 m²

they show the largest final spread and with values of 416 s / 424 s the fastest final stoppage time. FM1 shows the smallest final spread of 0.041 m² in combination with the longest final stoppage time of 500 s. The flow behaviour of mixture FM2 lays in between these two values with 0,043 m² and 448 s. As reported by L. Klein and O. Krause [7], the final stoppage time correlates with slump flow. Mixtures with lower viscosity will show a higher flow rate.

The correlation of viscosity with the increase of particle quantity, i.e. higher Vol.-% of raw material, in the mixture due to the lower density of the substituted fused mullite could explain these results. Mixture FM 1 contains 2.65 Vol.-%, FM2 1.61 Vol.-% and FM3 0.96 Vol.-% more raw material in this fraction than mixture REF.

Influence of the particle characteristics on the technological characteristics

Cold modulus of rupture and open porosity after drying are envisaged in Fig. 7. The reference material (REF) shows the highest strength and the lowest open porosity. The substitution of two coarse grain fractions (FM1) results in the lowest strength however, the open porosity is in the same range as the reference castable. If only one fraction is substituted (FM2 and FM3) the strength values are comparable with the reference castable but with a higher uncertainty. Here the open porosity is about one Vol.-% higher than for the reference castable.

The difference in CMoR could be primarily explained with the general lower CMoR values that are obtainable for mullite-based monolithics if they are compared with tabular alumina-based monolithics [10]. This is due to the described smooth surface of fused mullite that leads to a lower degree of interlocking of bigger particles with the matrix. In further mullite single crystals have a good cleavage that increases the trans-particle rupture under mechanical stress. FM1 contains the highest amount of fused mullite (32 wt.-%), and as it could be expected for this castable, it shows the lowest strength values.

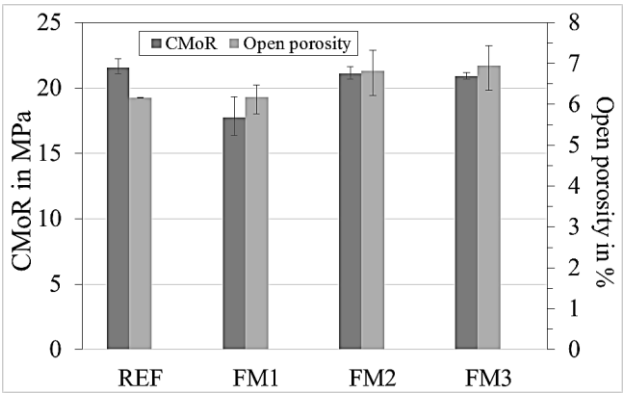

Figure 7. Cold modulus of rupture in MPa and open porosity in Vol.-% of the cement-bonded self-flowing high alumina castables (REF) and three self-flowing high alumina castables with grain fraction substitutions by fused mullite (FM1, FM2 and FM3).

However, it has also to be considered that the density of mullite is about 1 g/m^3 lower than that of corundum. If the same amount of corundum is substituted by mullite in weight percent the volume for these fractions increases in the castable. This influences the flow characteristics as visible for the slump-flow (fig. 6). Therefore, the low strength values as determined for FM1 can also be explained with an inferior densification during the moulding of the test pieces. The values for the open porosity underline the influence of the slump-flow character as a measure for the densification properties of the castable. All mullite containing castables show higher values than the reference castable.

CONCLUSION

In this early state of the project it is difficult to generalise the reported findings. In this first attempt the results of CPA show that the nature of the particles is too alike to figure out the influence of the particle shape on the working properties and the technological performance of the castable. However, it could be highlighted that grain size distributions calculated in weight percent bear the risk that in case of variable grain densities grain fractions are dosed not according to the optimal grain size distribution. This leads to a variation in the working properties that also show that highly dispersed refractory castables are sensitive even to minor changes.

Regarding the improvement of strength because of smart particle distribution in size and shape the CMoR values of the reference material cannot be compared with the substitution mixtures FM1 to FM3 due to the general difference of the TA and FM raw materials. To follow up this goal there are further investigations planned, where a substitution of the reference TA by TA with significant differences in particle shape and surface will take place.

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