Perceptions and Characteristics of Fused and Sintered Refractory Aggregates

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There are many perceptions in the market about the most appropriate refractory aggregate for a particular application. Opinions about the relative benefits of the fused and sintered versions of synthetic high alumina materials are set and often difficult to discuss and refute. But changes in the refractory raw materials market over the past few years have influenced the properties of the currently available synthetic high alumina materials and triggered the development of new aggregates. The purpose of this paper is to outline the differences between high alumina fused and sintered raw materials. The focus will be on physical properties such as density, porosity and grain shape, but the influence on the final properties of refractory formulations such as bricks, castables or dry vibratable mixes is also discussed (DVMs).

1 Introduction

The refractory community continuously strives for better and deeper understanding of materials, their reactions and applications. Studies conducted in the past, plus individual experiences, positive or negative, have created many perceptions in the market about the most appropriate refractory aggregate for a particular application.
With regard to the use of fused and sintered aggregates in both refractory bricks and castables, opinions are set and are difficult to discuss and refute. These include:

- Fused raw materials are more dense and therefore more resistant to corrosion
- Fused raw materials have a rounder grain shape that is better for densification and flowability
- Sintered aggregates are more reactive and develop higher strength during firing. Therefore the thermal shock resistance is lower when compared to fused aggregates.

However, something that applied in the past does not necessarily have to be still valid today.

Many changes have taken place in the refractory raw materials market over the past few years. Long-established production facilities have been shut-down and new ones built at strategically favourable locations. Short-supply and economic pressure have led to changes in certain production processes. Mines have been closed, other mineral deposits opened and new raw materials have been developed. Fused and sintered versions of most synthetic high alumina materials exist in the market. High alumina aggregates with > 99 % Al_2O_3 are white fused alumina (WFA) and sintered tabular alumina. Brown fused alumina (BFA) was for long time the only choice as a titanium-doped high alumina aggregate. With the development of BSA 96, an alternative sintered aggregate was introduced to the market in 2010 [1].
The purpose of this paper is to outline the differences between high alumina fused and sintered raw materials and show their influence on the final properties of refractory formulations. The focus will be on white and brown fused alumina and sintered Tabular alumina and BSA 96. Other aggregates such as Spinel and mullite also exist as fused and sintered versions but are not discussed in this paper.

2 Production of high alumina aggregates

2.1 Fusion process

Typically, white fused alumina (WFA) is produced by batch melting of a Bayer alumina feedstock in an electric arc furnace. After melting at temperatures >2000 °C, cooling of the blocks takes place and Na_2O is segregated as β-alumina ($Na_2O \cdot 11\ Al_2O_3$) in the upper central portion of the fused block. Due to the inherent cooling of the molten alumina block, WFA properties differ between the inner and the outer part of the block. Apart from the differences in Na_2O content, the crystal size and the open porosity also vary in different sections of the

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Tab. 1 Chemistry of BSA 96 by fraction

Chemistry [%] per Fraction [mm]						
	6–15	3–6	1–3	0,5–1	0–0,5	<90 µm
Na_2O	0,30	0,32	0,31	0,31	0,29	0,32
Fe_2O_3	0,15	0,14	0,15	0,15	0,15	0,14
SiO_2	0,91	1,10	1,06	1,04	0,95	1,08

Tab. 2 Comparison of open porosity and mean pore diameter of fused and sintered refractory aggregates

		Tabular Alumina	White Fused Alumina (WFA)		
		T60/T64	supplier A	supplier B	supplier C
		5–8 mm	3–5 mm	3–6 mm	3–6 mm
Mean pore diameter	[µm]	0,71	47,3	30,7	43,9
Open porosity	[vol.-%]	1,51	5,56	5,77	5,22
Bulk density	[g/cm³]	3,60	3,66	3,66	3,71

		BSA 96	Brown Fused Alumina (BFA)			
			supplier A	supplier B		supplier C
		5–8 mm	3–5 mm	3–6 mm	6–10 mm	3–6
Mean pore diameter	[µm]	0,38	28,0	14,7	27,0	24,9
Open porosity	[vol.-%]	4,40	0,85	1,84	1,99	1,24
Bulk density	[g/cm³]	3,52	3,88	3,88	3,85	4,00

block. Careful selection of the various WFA grades is required to separate low purity WFA and the small crystal size fused alumina from the higher quality portion.

Brown fused alumina is produced by fusing pre-calcined non-metallurgical bauxite in a batch or semi-batch furnace. During the fusion process oxides of silicon and iron are reduced to metal by the addition of coke and are removed as ferrosilicon. Iron scrap is added to facilitate the gravimetric separation of ferrosilicon [2].

A shortening of the melting and separation process in order to reduce production cost will have a significant impact on the quality of the fused product. Unless the fusion process is carefully controlled, the product may contain residual carbides, metallic inclusions and other impurities.

2.2 Sintering process

The production of sintered high alumina aggregates such as tabular alumina and BSA 96 follows the same process steps as practised in the advanced ceramics industry. In principle, they consist of raw material grinding, forming, drying and sintering. Initially, fine-crystalline alumina feedstock is ground in a ball mill. In order to get aggregate and powder sizes as required by the refractory producers, it is necessary to agglomerate the ground feedstock prior to the sintering. This is done in a granulation process, in which balls of 25 to 30 mm diameter are formed. The green balls are then rapid-sintered in a vertical shaft kiln at temperatures in excess of 1800 °C under a neutral to oxidizing atmosphere. The final step after cooling of the sintered balls is crushing and screening of the balls to specific aggregate sizes. Intensive magnetic de-ironing is incorporated into the process to remove iron contamination in the final products [3].

3 Chemical purity

The impurity levels of fused and sintered aggregate are generally similar. The major difference is the location of the impurities. Because of the ceramic processing the impurities of sintered aggregates are homogenously distributed within the structure. As a consequence all size fractions have the same chemical composition as shown in Tab. 1. Even the fine milled materials have the same chemical composition as coarser fractions.

This is different to fused aggregates where impurities often accumulate in the fine fractions. These impurities may react with water and have a negative impact on the flow and setting behaviour of castables or influence the sintering behaviour as described by Büchel et.al. [4].

3 Density and Porosity

It is often stated that fused grains show a better chemical resistance when compared to sintered aggregates of similar chemical composition due to high density, low open porosity and large crystal size.

White and brown fused alumina samples of different origin (European and Chinese) and Tabular alumina and BSA 96 were tested at the DIFK, Höhr-Grenzhausen by using the mercury-intrusion method in accordance with DIN 66133. The bulk density, open porosity and mean pore diameter are shown in Tab. 2 and the pore size distribution (relative pore volume) in Fig. 1 a-d.

The bulk density and the open porosity of all WFA samples is higher than for tabular alumina. This can be attributed to the differences in microstructure between fused and sintered alumina. (Fig. 2)

The ceramic sinter process permits a well-controlled development of microstructure where small pores are entrapped inside and between the crystals. These pores are mainly closed and are the reason for the lower bulk density and lower open porosity of tabular alumina. However, even more important than the absolute value of open porosity is the difference in the mean pore diameter between WFA and tabular alumina. The average pore size of the tested white fused alumina varies between 30,7–47,3 µm whereas tabular alumina exhibits a mean pore diameter in the submicron range of 0,71 µm. As shown in Fig. 1 a-d in Tabular alumina there are virtually no pores present with a diameter larger than 10 µm.

Brown fused alumina has a significantly higher bulk density and slightly lower open porosity by mercury intrusion method when compared to BSA 96. But the mean pore diameters for the brown fused samples range between 14,7–28,0 µm whereas the mean pore diameter of BSA 96 is only 0,38 µm.

The total open porosity of a refractory material is a critical value, because open pores increase the surface area of the refractory material that can be attacked and

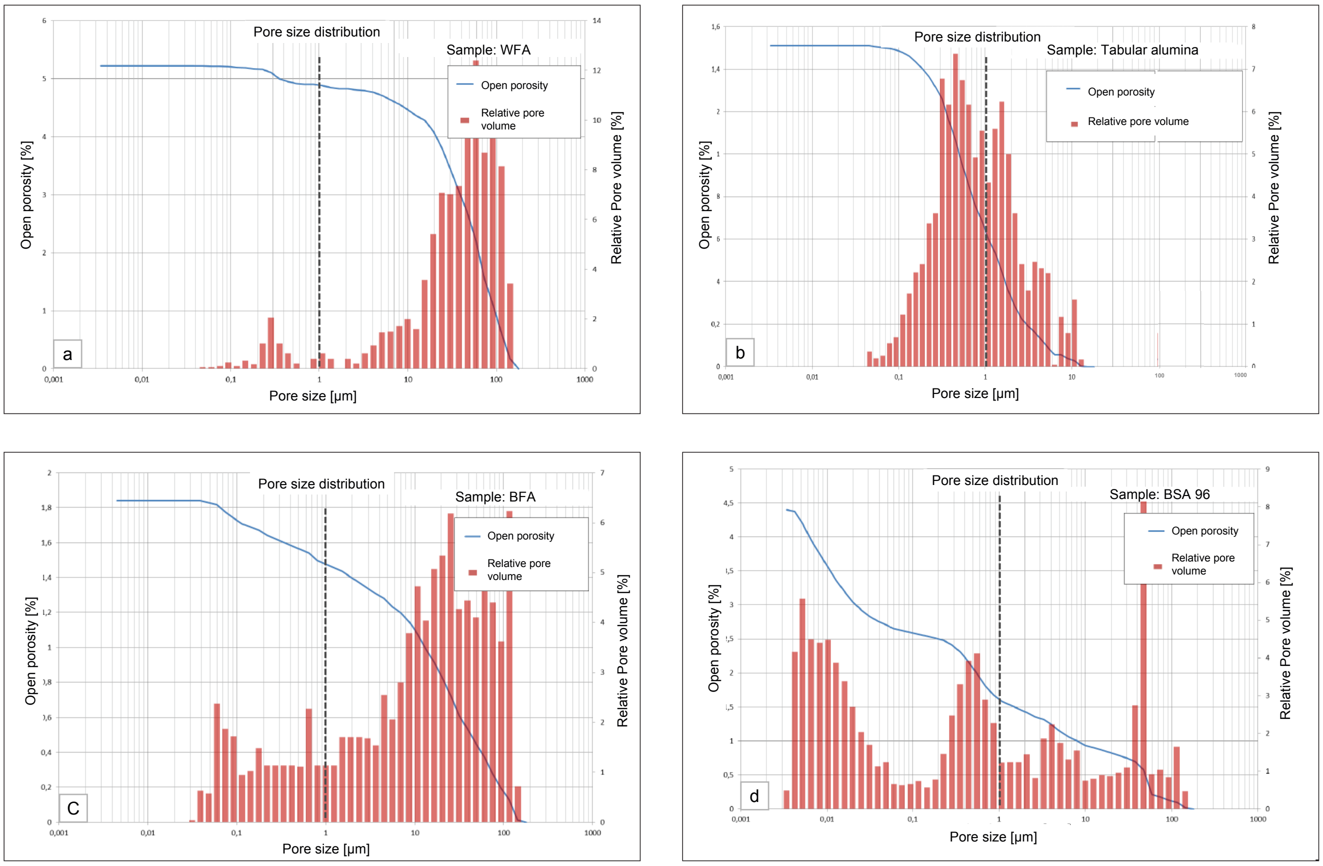

Fig. 1 Pore size distribution of fused and sintered high alumina aggregates: a) WFA; b) tabular alumina; c) BFA; d) BSA 96

will therefore contribute to accelerated corrosion. However the pore size is also important in order to judge the resistance of a material against corrosion. As shown by Borovikov the calculated infiltration speed of a pore with a size of 50 µm by a typical steel slag is more than 100 times higher than for a pore of 1 µm [5].

Small pores <1 µm can almost not be infiltrated by typical steel slags or metals and do not therefore support corrosion by offering additional surface area.

Although the bulk density of fused aggregates is generally higher than for the comparable sintered aggregate their porosity is mainly open with large pores that can be easily penetrated. Tabular alumina and BSA 96 show a clear advantage over fused materials with regard to corrosion because of their closed porosity and the very fine pore structure of the open pores.

The closed porosity of sintered high alumina aggregates is also the reason for their good thermal shock resistance when compared to fused materials. The pores prevent the propagation of cracks which have been generated by the thermo-mechanical stress induced by the thermal shock. As described in previous papers the percentage of undamaged grains of Tabular alumina after 20 thermal shock cycles is four to five times higher than for fused aggregates with comparable chemical composition [3].

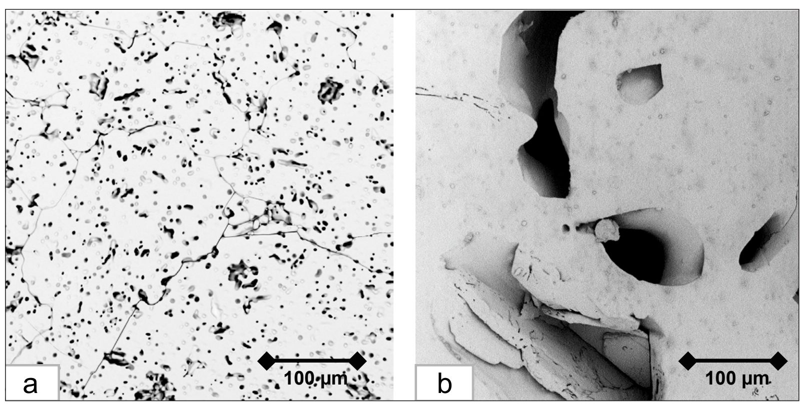

Fig. 2 Microstructure of tabular alumina (a) and white fused alumina (b)

3.1 Grain shape

The grain shape of fused and sintered high alumina aggregates was measured with an optical analyser, CAMSIZER P4 using Dynamic Image Analysis (DIA) from Retsch Technology. DIA analyses the shadow projections of particles and a variety of size parameters can be measured.

For this study the focus was on:

- Aspect or width/length ratio, as a function of the largest diameter and the smallest diameter at right angles to it. With increasing aspect ratio the grains are rounder; low values indicate elongated, splintery grains.
- Sphericity or circularity as described in ISO 13503-2

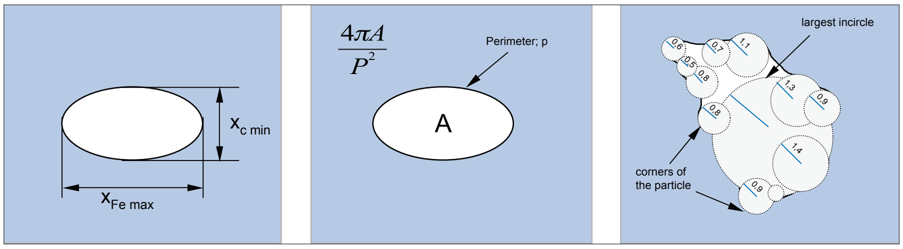

Fig. 3 Shape parameters: width/length ratio (l.), sphericity (middle) and corner roundness (r.) [7]

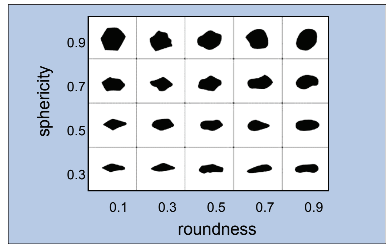

Fig. 4 Krumbein and Sloss table [7]

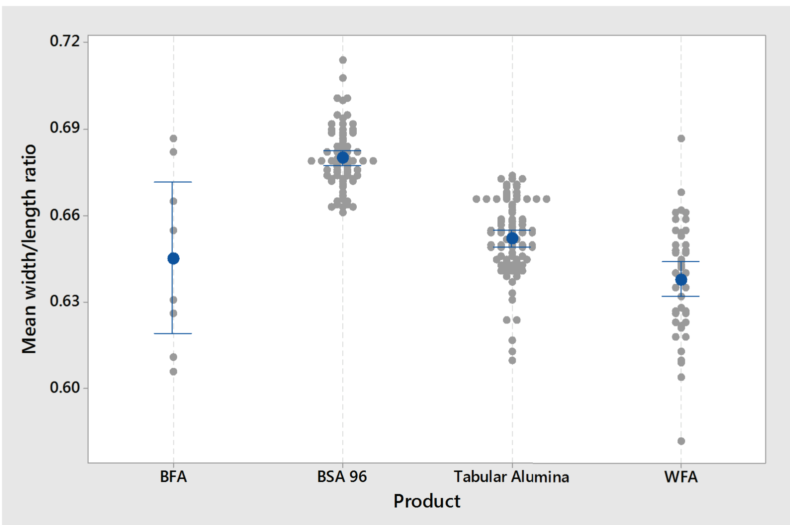

Fig. 5 Mean aspect ratio of fused and sintered refractory aggregates

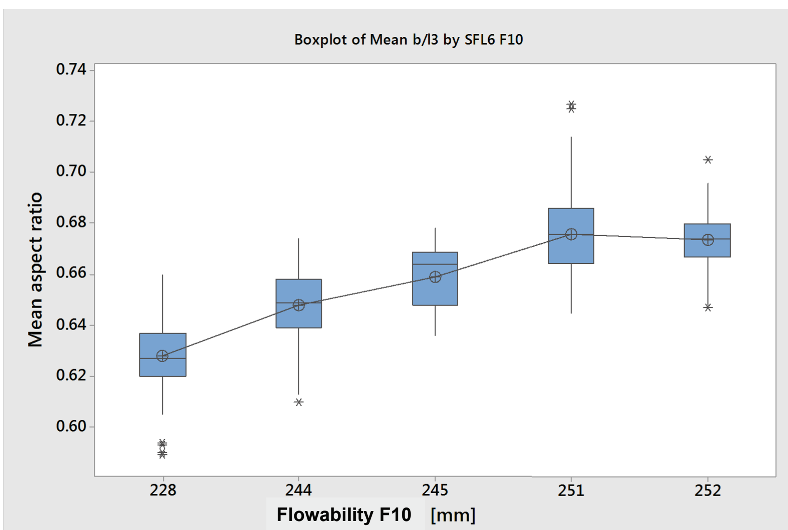

Fig. 6 Relationship of aspect ratio of refractory aggregate to flowability of a self- flowing castable

- Corner roundness as mean radius of all corners divided by the radius of the largest incircle. Higher values indicate a smoother surface whereas sharp-edged particles have typically low values (Fig. 3).

A well-established method for determination of the shape of sand and sediments in geological analyses is the manual analysis of roundness and sphericity according to Krumbein and Sloss. The corner roundness on the X-axis is plotted against the sphericity on the Y-axis, and therefore allows a more complex description of the particle shape. Particles with high corner roundness and sphericity such as glass beads lie in the upper right corner of the Krumbein & Sloss table shown in Fig. 4. Sharp-edged, elongated particles are in the lower left corner.

As shown in Fig. 5 the average aspect ratio of WFA, BFA and Tabular alumina are very close – 0,64 for the fused aggregates and 0,65 for sintered alumina. BSA96 shows a slightly higher average aspect ratio of 0,68 representing more cubic shaped grains.

The influence of these apparently small differences of the grain shape on the flowability of a refractory castable is shown in Fig. 6. Selected tabular fractions with different aspect ratios from 0,62 to 0,68 were tested in a formulation of a self-flowing castable. Particle size distribution and matrix composition were kept constant. The flowability was measured 10 min after mixing.

For the same water content the flowability improves from 228 mm to 252 mm with an increase of the aspect ratio from approx. 0,63 towards more cubic particles with an aspect ratio of approx. 0,68.

The analysis of the size parameter according the Krumbein & Sloss table even better illustrates the differences between fused and sintered refractory aggregates.

The mean sphericity of the tested WFA has a wide spread from below 0,52 to 0,66. The two visible major areas can be attributed to the different suppliers of the material. All WFA samples have a low mean roundness below 0,3 which means sharp-edged grains. As the primary application of these aggregates is in the abrasion market, this property is required to achieve good cutting results.

The size parameters of tabular alumina almost overlap with those of the more rounded WFA samples. A slight shift can be noticed in corner roundness which is on average higher for the sintered aggregate. The origin for this may well be in the microstructures which result in different fracture behaviour.

The BSA 96 results are positioned more in the upper right corner of the chart which represents the roundest grains with the smoothest surface of the tested materials. The BFA results are wide spread for both sphericity and roundness, but there are not enough data points to draw sound conclusions. It seems that as in the case of WFA the shape parameters for BFA are also much dependent on the supplier.

4 Sinter reactivity

Various studies have been conducted to compare the differences in reactivity of fused and sintered aggregates. The following are excerpts from these studies. Additional and more detailed information can be found in the original publications.

4.1 AluMagCarbon (AMC) bricks

AMC bricks consist of an alumina aggregate, calcined alumina, magnesia and carbon e.g in the form of graphite and resin binders. During use, AMC bricks expand at the hot face due to a spinel formation, which results in reduced wear in the joints between the bricks.

The influence of the alumina aggregate on the spinel formation during firing and on the final brick properties of AMC bricks have been investigated by Klewski et al. [8]. The test brick formulations were based upon four different high alumina aggregates WFA, tabular alumina, BFA and BSA 96. Magnesia content and matrix formulation were identical for the first test series.

Distinct differences were observed in the permanent linear change (PLC) between the BFA and BSA 96 bricks after firing. BSA 96 shows a stronger increase of PLC above 1300 °C when compared to BFA.

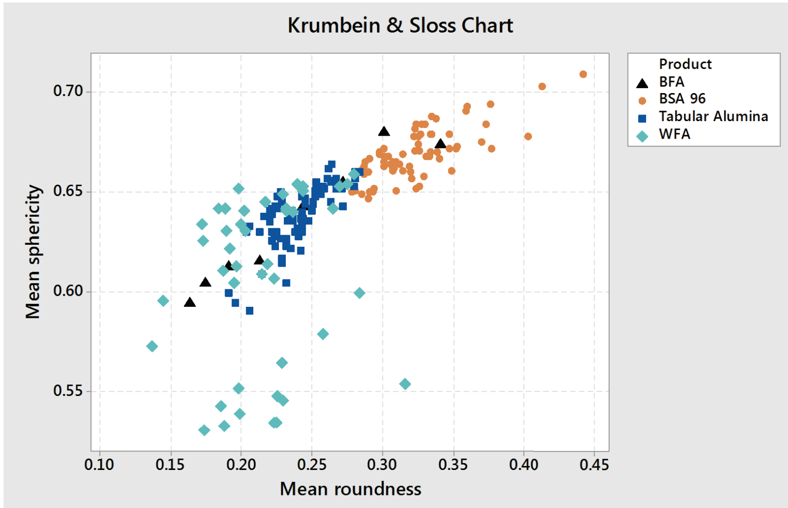

Fig. 7 Krumbein and Sloss chart of fused and sintered refractory aggregates

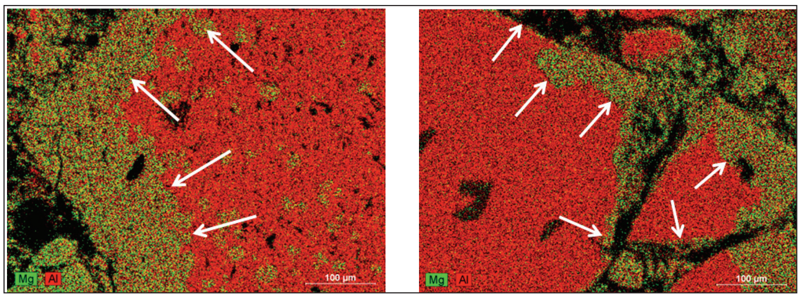

Fig. 9 EDX of BSA 96 (l.) and BFA (r.) grains in AMC brick fired at 1600 °C/5 h in reducing conditions

At 1600 °C the expansion with BSA 96 is 2,7 %, but with BFA it is 2,1 % (Fig. 8).

Mineralogical investigations of the fired bricks show a more intense and homogeneous spinel formation with the sintered BSA 96 (Fig. 9).

Spinel formation with tabular alumina is also quicker than for WFA as seen in the rise of the PLC curve above 1400 °C. In general the spinel formation of these high purity materials starts at higher temperatures when compared to BFA and BSA 96. This proves the influence of traces of impurities on the spinel formation.

Sintered aggregates show an earlier and more even spinel formation in AMC bricks when compared to fused aggregates due to their higher sintering activity. BSA 96 contains less and more evenly distributed impurities than BFA. Therefore BSA 96 shows predictable and consistent behaviour in spinel formation and PLC. Expansion be-

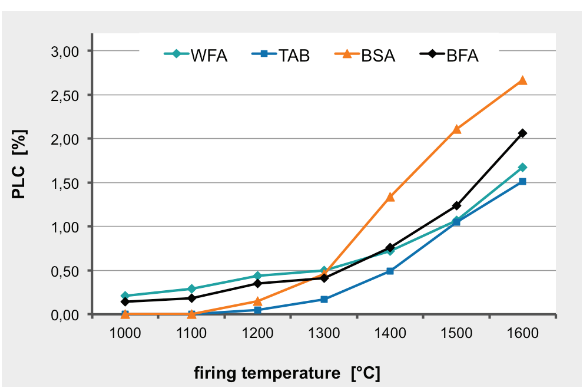

Fig. 8 Permanent linear change of AMC bricks, fired under reducing conditions for 5 hours

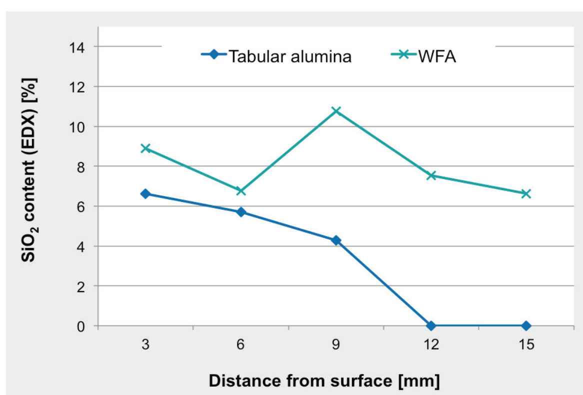

Fig. 10 Slag penetration in high alumina brick; measured by EDXA [6]

Tab. 3 Different DVM formulation concepts and results

		Mix 1	Mix 2	Mix 3
White fused alumina	0–3 mm	81		
Tabular alumina	coarse		65	72
	fines		16	11
Calcined alumina + sintering aid		7	7	7
MgO		12	12	10
Grain density [g/cm³]		3,70	3,55	3,55
Rammed density [g/cm³]		2,80	2,64	2,71
Densification [%]		75,7	74,4	76,3
PLC [%]		5,4	6,9	5,5
CCS [MPa]		9,8	6,5	9,1

haviour and thermo-mechanical properties can be by adjustment of magnesia content of the bricks.

4.2 Dry vibration mixes

Induction furnaces for high quality alloy steel casting at high temperatures and with long residence time require high corrosion resistant lining materials. Spinel forming alumina dry vibrations mixes (DVMs) are the typical lining solution. These mixes are installed in the dry form by compaction via vibration/ramming. This is followed by an initial sintering step to achieve sufficient strength in the front layer.
The basic challenge in the formulation of these type of refractory materials is to accelerate the spinel formation in the front layer during the first melt to protect the lining against early wear, but also to keep a less sintered powder zone at the back of the lining for safety purposes.
Chatterjee et al. presented a study where high purity fused and sintered alumina aggregates are compared in spinel forming DVMs [9].
White fused alumina and tabular alumina were tested in the mixes detailed in Tab. 3.
For mix 2 only the aggregate was changed and the particle size distribution of the Tabular alumina fractions adjusted to take into account the differences in bulk density of WFA (around 3,70 g/cm³) and tabular alumina (around 3,55 g/cm³). Although the rammed density of the tabular alumina mixes is lower, the densification level for tabular alumina is comparable to WFA. This proves that, contrary to what is often claimed, the particle shape of WFA does not allow better densification. As mentioned above the aspect ratio of particular cubic WFA and Tabular alumina are almost identical.
After firing at 1600 °C for 3 h, the expansion of tabular alumina mix 2 is much higher at 6,9 % when compared to WFA at only 5,4 %. As a consequence the cold crushing strength (CCS) is reduced.
This confirms the higher thermal reactivity of tabular alumina compared to that of WFA. Mineralogical analysis by XRD of mixes 1 and 2 found no spinel formation at 1000 ˚C, but a significantly higher amount for mix 2 at elevated temperatures (1200–1600 ˚).
For mix 3 the reactive components of the spinel formation, tabular alumina fines and MgO, were reduced to control the overall reactivity and to achieve similar expansion levels as obtained with the fused aggregate. The adjustment of the recipe resulted in similar physical properties for a mix based on sintered aggregate to the traditionally used white fused alumina.

4.3 High alumina bricks

High purity corundum bricks are widely used in industrial furnaces such as oil cracking units. Critical properties are chemical corrosion resistance, abrasion resistance and thermo-mechanical stability.
Studies conducted at the Luoyang Institute of Refractories Research (LIRR) in China, compared high purity corundum bricks based on Tabular alumina and white fused alumina as single aggregates and also a combination of both aggregates [6].
Due to the higher reactivity of sintered aggregates, the tabular alumina containing bricks show much higher density, lower apparent porosity, higher compressive and tensile strengths than WFA bricks at identical firing temperatures.
In corrosion tests with oil cracking slag, the tabular alumina bricks outperformed WFA based bricks. The slag penetration, represented by the silica content rapidly decreased and, for the tabular alumina brick, was almost zero at a depth of 12 mm. The WFA brick still had significant infiltration even further into the brick. This result can be explained by the better densification in addition to evenly distributed small pores and a good link between matrix and sintered grains. The strong interconnection of sintered aggregates and matrix also results in an improved abrasion resistance of the Tabular alumina bricks when compared to the white fused alumina bricks. The abrasion loss according to ASTM C704 was 4,4 cm³ for tabular alumina but 8,7 cm³ for WFA.

5 Conclusion

The manufacture of high-alumina aggregates generally reqires significant energy input to make the highly refractory feedstock react. Established technologies are the fusion process and the sinter route. Producing fused alumina with an electric arc furnace in itself is a very energy intensive process. Sinter processes run at lower energy levels. Considering the overall impact of high energy consumption and the corresponding impact on greenhouse gas emissions, it becomes obvious that the sinter process is the more sustainable process route for the manufacturing of high alumina aggregates.
The different process routes of fusing and sintering do not only influence the energy balance of the manufactured raw material but also have an impact on the material properties of the high alumina aggregates.
In general it can be stated that depending on the cooling conditions and the quality of the grading process, fused aluminas are more inhomogeneous products when compared to the sintered aggregates. The sintering process route enables both a homogeneous distribution of the impurities in the product and stable physical properties, e.g. density, porosity and microstructure.

"Fused raw materials are denser and thus more resistant to corrosion"
The bulk density of fused aggregates is generally higher than for comparable sintered

aggregates, but their porosity is mainly open with very large pores of >50 µm. Sintered aggregates exhibit high closed porosity and very fine open pores of less than 1µm that can hardly be penetrated by corrosive media. The lower bulk density is even an economic advantage as less material is required for a given application.

"Fused raw materials have a more roundish grain shape that is better for densification and flowability"

The grain size parameters of tabular alumina and WFA overlap over a wide range. Some white fused aluminas are even more splintery than the sintered aggregate. This was also shown by identical densification levels in sensitive dry vibrating mixes. BSA 96 has the roundest grains of the tested refractory aggregates and also the highest corner roundness.

"Sintered aggregates are more reactive and develop higher strength during firing. Therefore the thermal shock resistance is lower when compared to fused aggregates"

Sintered aggregates such as tabular alumina and BSA 96 are more reactive than fused aggregates of similar chemistry. In AMC bricks and dry vibrating mixes sintered aggregates show an earlier and a more even spinel formation when compared to fused aggregates. To reduce excessive expansion of the refractory materials adjustment of the recipes is required. Typically slight modifications, especially in the matrix, are sufficient to lower expansion reactions to a level similar to the one observed with fused aggregates. The earlier spinel formation can also be used to achieve a moderate spinel formation over a wider temperature range.

The better interconnection of the matrix with sintered aggregates increases the abrasion resistance of high alumina bricks and improves the penetration of slag.

The influence of the higher reactivity on thermal shock resistance is not yet clear. Initial trials with high purity alumina castables and high alumina bricks did not confirm superior behaviour of fused aggregates. It appears that it may well be the design of the matrix that has a significant role in the thermal shock resistance. Further studies are ongoing.

References

[1] Amthauer, K.; Buhr, A.; Schnabel, M.; Freundlich, S.; Dutton, J.: New European Sinter Aggregate with 96 % Al_2O_3, 54. International Colloquium on Refractories, Aachen, 2011, 95–98

[2] Cichy, P.: Fused Alumina – pure and alloyed – as abrasive and refractory material, in Alumina science and technology handbook ed. by L.D. Hart, American Ceramic Society, ISBN0-916094-33-2 (1990) 393–426

[3] MacZura, G.: In Alumina science and technology handbook ed. by L.D. Hart, American Ceramic Society, ISBN0-916094-33-2 (1990), 109–170

[4] Büchel, G; Liu, X.; Buhr, A.; Dutton, J.: Review of Tabular Alumina as High Performance Refractory Material. Interceram Refractories Manual 2007; 6–12

[5] Borovikov, R.: Dissertation; TU Freiberg „Untersuchungen zum Verschleiß hochtonerdehaltiger Feuerfestmaterialien für die Pfannenmetallurgie im Stahlwerksbetrieb; 2002

[6] Liu, X.; Yanqing, X.; Keming, G.; Buhr, A.; Büchel, G.: Tabular Alumina for High Purity Corundum Brick. The 5th International Symposium on Refractories (ISR'2007)

[7] http://www.retsch-technology.com/rt/applications/technical-basics/particle-shape/

[8] Klewski, M.; Maracha, G.; Buhr, A.; Schnabel, M.; Dutton, J.: Spinel formation and technical properties of AluMagCarbon bricks with different alumina aggregates. UNITECR 2015

[9] Shankha Chatterjee, A.; Buhr, A.; et al.: Role of tabular alumina as a suitable aggregate for emerging applications – focus on dry ramming mix. IREFCON 2014, 97–103