Five Years after Market Launch – Experiences with BSA 96

M. Schnabel, S. Klaus, A. Buhr, D. Schmidtmeier, J. Dutton

In 2011 Almatis introduced a new high alumina sintered aggregate to the market – BSA 96. The idea was to offer a European alternative to other high alumina aggregates – fused, natural or sintered. This paper will present a brief overview of the special characteristics of BSA 96 and describe the experience over the past five years using BSA 96 in various applications such as AMC bricks, high alumina bricks and blast furnace runner castables. Special focus will be on the formation of so-called CAM phases found in sintered castables with BSA 96 as the matrix component together with fine spinel and cement.

Tab. 1 Physical and chemical properties of BSA 96

Chemical composition	Min.	Max.	typical
Al_2O_3 [%]	95,5		97,0
TiO_2 [%]		2,0	1,5
SiO_2 [%]		1,0	0,5
MgO [%]			0,2
Na_2O [%]			0,30
Fe_2O_3 [%]			0,15
$Fe_{mag.}$ [%]		0,02	
Physical properties			**typical**
Bulk Specific Gravity [g/cm³]			3.5
Open Porosity [Vol.%]			4.5
Water absorption [mass%]			1.3

Tab. 2 Impurity levels of different BSA 96 fractions

	Fraction [mm]					
	6–15	3–6	1–3	0,5–1	0-0,5	<0,09
						
Na_2O	0,28	0,31	0,29	0,32	0,27	0,30
Fe_2O_3	0,16	0,18	0,20	0,21	0,19	0,16
SiO_2	0,54	0,58	0,62	0,61	0,51	0,51

1 Introduction

Brown Fused Alumina (BFA) was for many years the only choice as a titanium-doped high alumina aggregate. Supply issues with imported raw materials combined with continuous quality problems had triggered the development of an alternative high alumina aggregate. BSA 96, a new sintered aggregate was introduced to the market in 2011 by Almatis. This high alumina aggregate is produced in Europe and is independent from Chinese raw materials [1].

Since its launch, many customers have been sampled with BSA 96. Qualification testing in the laboratory and on site convinced those customers of the potential of this new aggregate. Today, BSA 96 has found its place in the European refractory industry and is an established refractory raw material for various applications such as high alumina bricks, alumina magnesia carbon (AMC) bricks and monolithics.

2 BSA 96 – Properties

2.1 Chemical composition

BSA 96 is a refractory aggregate with an Al_2O_3 content greater than 96 %. The major impurities are SiO_2, TiO_2 and smaller amounts of Na_2O and MgO (Tab. 1). It is important to mention that because BSA 96 is produced by the sinter process, all size fractions have the same chemical composition (Tab. 2). The firing of BSA 96 takes place under a neutral to oxidising atmosphere. Later in the process strong magnetic de-ironing removes iron particles which are introduced during the crushing and sizing of the fractions. As a consequence BSA 96 does not contain carbides or metallic components that could harm sensitive bonding systems. This is different to fused aggregates where impurities often accumulate in the fine fractions. These impurities may react with water and have an adverse effect on the flow and

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Tab. 3 Comparison of open porosity and mean pore diameter of BSA 96 and BFA

BSA 96		
Mean pore diameter	[µm]	0,38
Open porosity	[Vol.-%]	4,40
Bulk density	[g/cm³]	3,52

BFA		
Mean pore diameter	[µm]	14,7 – 28,0
Open porosity	[Vol.-%]	0,85 – 1,99
Bulk density	[g/cm³]	3,85 – 4,00

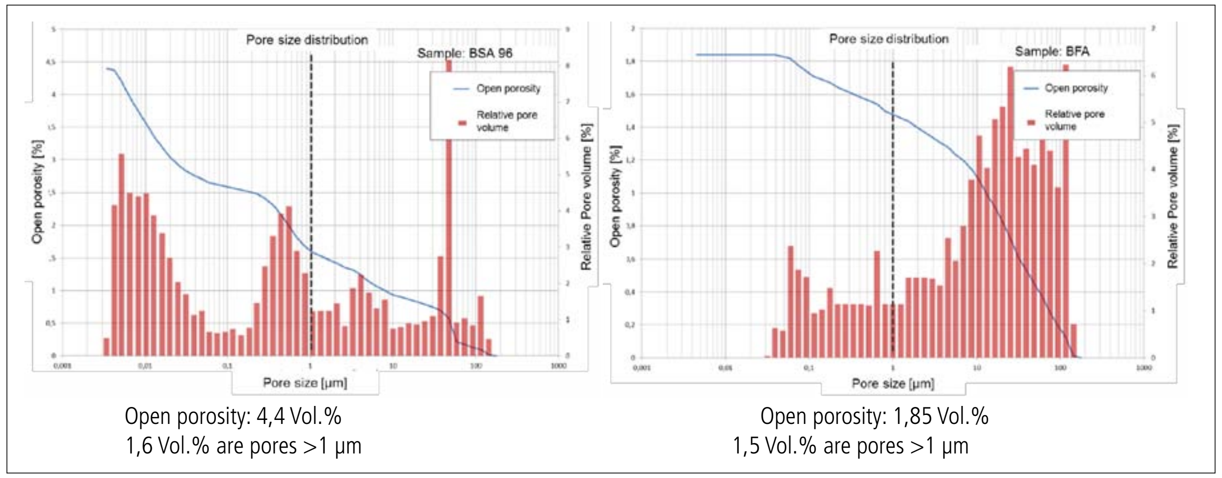

Fig.1 Pore size distribution of BSA 96 and BFA

Fig. 2 New crushing centre at Almatis Ludwigshafen plant

setting behaviour of castables. They could also negatively influence the refractory performance of bricks and the appearance of fired pieces by melted spots or blisters on the surface.

2.2 Physical properties

The sintered high alumina aggregate BSA 96 has a similar bulk density to tabular alumina. Water absorption and open porosity are also in the same range (Tab. 1). The bulk density of BSA 96 is lower when compared to brown fused alumina. This is a typical feature of sintered aggregates. 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 low open porosity of BSA 96 [2].

However, even more important than the absolute value of open porosity is the difference in the pore diameter. The mean pore diameter of BSA 96 is only 0,38 µm whereas the mean pore diameter for brown fused alumina samples ranges between 14,7–28,0 µm (Tab. 3).

It is important to note that according to literature, small pores <1 µm can almost not be infiltrated by typical steel slags or metals and do therefore not support corrosion by offering additional surface area [3].

Although the open porosity of BSA 96 is slightly higher than the porosity of brown fused alumina, the total volume of accessible pores >1 µm is identical for sintered BSA 96 and brown fused alumina (Fig. 1).

3 BSA 96 production – committed to long-term supply

With the introduction of BSA 96 Almatis invested more than USD 6 million in a new crushing centre at its German facility in Ludwigshafen to avoid cross-contamination of established products such as Tabular alumina and Spinel. Ground-breaking for the expansion project took place on 7 June 2011 and the plant has been in full production since January 2012 (Fig. 2).

The general production process of BSA 96 is identical to the production of tabular alumina and sintered spinels, which is described in detail by MacZura [4].

The sintering process route enables both a homogeneous distribution of the impurities in the product, and also stable physical properties, e.g. density, porosity, and microstructure. No carbides or metallic components are formed during the sintering 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.

Today, BSA 96 is produced in 8 different sizes to meet various customer requirements (6–15 / 3–6 / 1–3 / 0–1 / 0,5–1 / 0–0,5 / 0–0,2 / <90 µm). Coarse fractions of 6–15 mm are used in pre-cast fabrications such as EAF-roofs and lances to give improved thermal shock resistance. Fine milled fractions and powders such as <90 µm and 0–0,2 mm are advantageous, especially in phosphate bonded ramming mixes and mortars, due to their low metallic iron content.

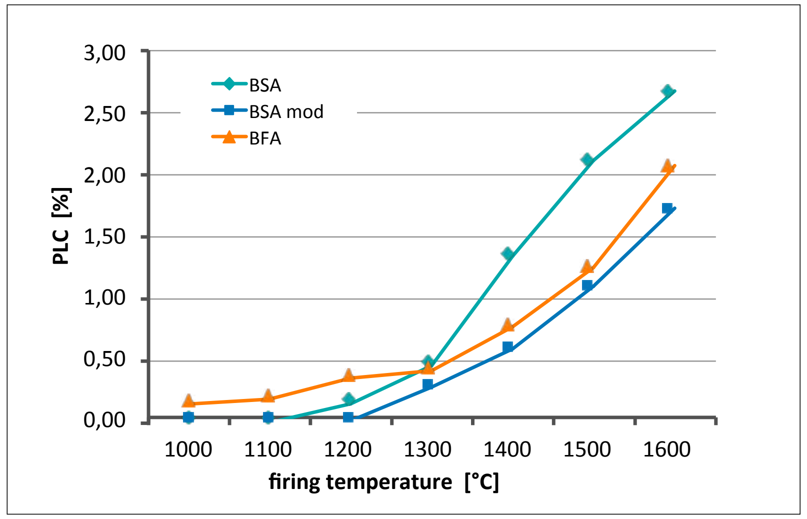

Fig. 3 Permanent linear change of AMC bricks, fired under reducing conditions for 5 h

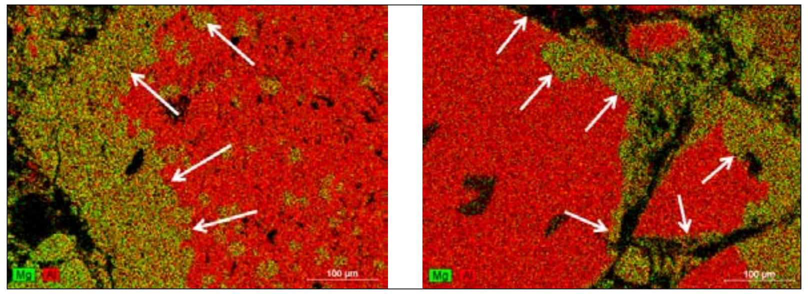

Fig. 4 EDX of BSA 96 (l.) and BFA (r.) grains in AMC brick fired at 1600 °C/5 h in reducing conditions; arrows indicate the spinel layer formed during firing

4 BSA 96 – refractory applications

Close to two thirds of the volume of BSA 96 supplied today is used in castables and other monolithic mixes as a replacement for brown fused alumina or as an up-grade for bauxite-based materials. Typical mixes are the so-called "black castables" for blast furnace runners and cupolas. Brown and white fused aluminas in brick formulations were also successfully replaced by BSA 96.

4.1 AluMagCarbon (AMC) bricks

AMC bricks consist of an alumina aggregate, which is typically bauxite or brown fused alumina, calcined alumina, magnesia and carbon, normally in the form of graphite, plus resin binders. During use, AMC bricks expand at the hot face due to spinel formation. This results in reduced wear in the joints between the bricks.

Intensive testing and qualification of BSA 96 has been done at Arcelor Mittal Refractories in Poland. The influence of alumina aggregate on spinel formation during firing and on the final brick properties of AMC bricks has been investigated and the results are reported by Klewski. et al. [5].

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. 3).

Mineralogical investigations of the fired bricks showed that the spinel formation is more intensive and more homogeneous with BSA 96 than with BFA due to more evenly distributed impurities and the small, homogeneously distributed pores in the structure of the sintered aggregate (Fig. 4).

The expansion was adjusted by slightly reducing the magnesia content of the formulation and a BSA 96 based AMC brick was developed and successfully tested in practice.

Predictable expansion behaviour (PLC) of AMC bricks during use is essential for good performance in the steel ladle.

BSA 96 provides stable raw material properties, which enable smoother and controlled production and predictable and reliable performance.

4.2 Castables for blast furnace runners

Low cement and ultra-low cement castables with 60–85 mass-% Al_2O_3 and 5–25 mass-% SiC are used for the wear lining in the blast furnace main trough. Brown fused alumina is the most common aggregate for these castables although in some cases tabular alumina is also used.

For many years refractory producers have had to cope with wide variations in the quality of Chinese brown fused alumina. The availability of a more stable raw material for these quite complex and also sensitive formulations triggered a very rapid deployment of BSA 96 in first test castables (Fig. 5).

Because of the density differences between BSA 96 (3,50 g/cm³) and BFA (3,8 g/cm³) some recipe adjustment was required in order to achieve the same particle size distribution of the castable. The castable densi-

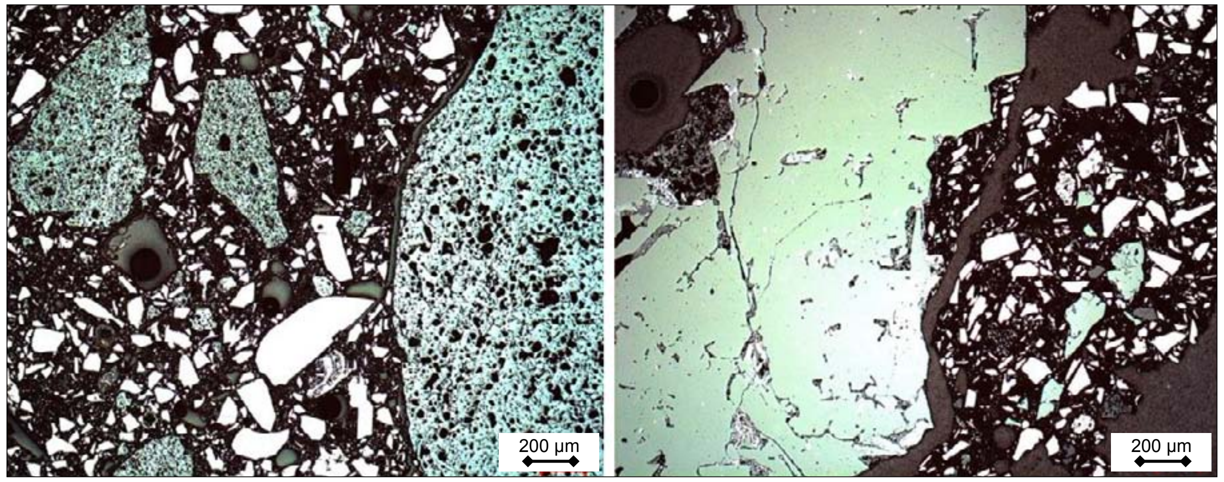

Fig. 5 Comparison of BSA 96 (l.) and BFA (r.) containing castable for blast furnace runners ("black castable")

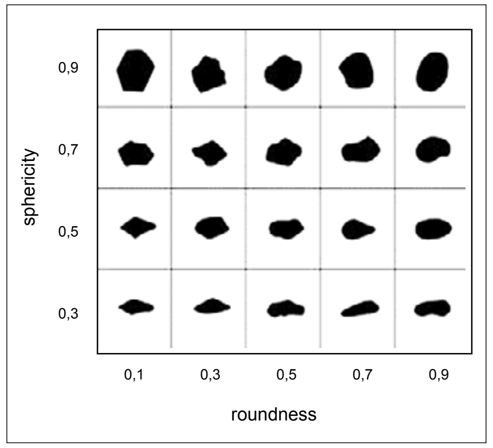

Fig. 6 Krumbein and Sloss chart [7]

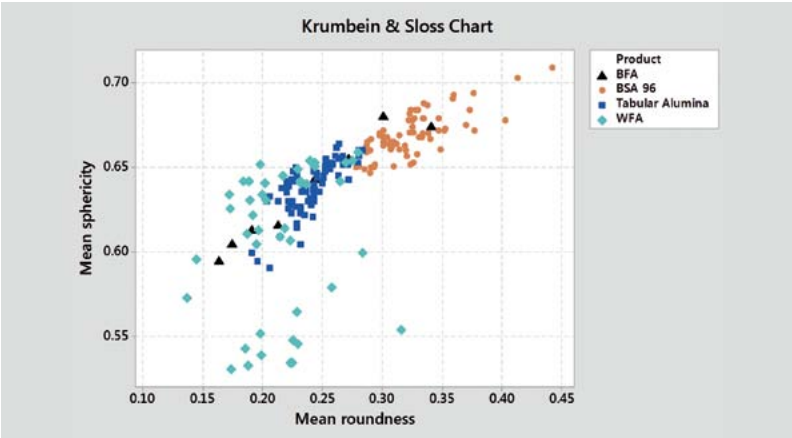

Fig. 7 Krumbein and Sloss chart of fused and sintered refractory aggregates

ties were found to be 3–5 % lower for the BSA 96 based mixes. Assuming the same performance level, this density difference translates directly to financial savings for a given installation.

It was also noticed, that the replacement of BFA by BSA 96 leads to a changed cement setting (EXOmax). The matching of cement setting and Al-reaction needed to be adjusted. This could easily be achieved by dispersing aluminas ADS 3 and ADW 1. Once completed, the BSA 96 based formulations show very stable setting behaviour when compared to the BFA based formulation. This is most likely explained by the low and homogeneous impurity levels of the sintered aggregate.

Under laboratory conditions the strength values after drying and firing were found to be similar for both formulations. Feedback from on-site installations reported that the BSA 96 based castables were easier to clean out. Therefore less good material was removed during cleanout and less repair material was required.

The use of BSA 96 in castables for blast furnace runner mixes showed at least similar corrosion resistance when compared to the BFA based mixed. The lower castable density and easier cleaning contribute to a reduced specific consumption of castable per ton of iron and therefore to a more economical solution for the refractory producer.

4.3 High alumina bricks

One of the first applications for BSA 96 in bricks was the new development of a fired brick for applications under reducing conditions. Only CO-resistant refractory raw materials are suitable aggregates for the formulation of bricks to be used in such an environment. Iron or iron oxide contamination in refractory raw materials destroys the CO resistance. The metallic iron content of BSA 96 is only maximum 200 ppm. The newly developed fired brick based on BSA 96 was tested for CO resistance according to ASTM C288-87 in a CO atmosphere with >95 % CO at 500 °C for 200 h. The BSA 96 brick was rated class A (best achievable) [6].

The very low metallic iron content of BSA 96 also provides improved brick surfaces without any blisters or spots. This is not just a cosmetic reason, because a clean surface of the fired brick also reduces interruptions of the mostly automated production process due to the risk of bricks sticking together and increases the yield in production.

For the production of pressed bricks the grain shape of the aggregate, amongst other factors, is important for good compaction during pressing. Typically, rounder grains require less pressure to achieve the same density than splintery shaped grains. At a given capacity of the press, rounder aggregates could help achieve higher and more homogeneous pressed densities of the bricks.

A well-established method for determination of aggregate shapes is the manual analysis according to Krumbein and Sloss (Fig. 6). The corner roundness is plotted on the x-axis against the sphericity on the y-axis. This 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 and Sloss table. Sharp-edged, elongated particles are in the lower left corner.

The grain shape of typical high alumina aggregates are shown in Fig. 7. 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. Feedback from customers who have changed their brick formulations to include BSA 96 have confirmed a more stable and smooth production of bricks which are based on BSA 96.

4.4 High-purity low cement castables

The offer of a stable, homogeneous sintered aggregate also triggered some recipe changes in high alumina castables used in various other applications such as aluminum melting furnaces, steel lances or EAF-roofs.

Coarse BFA fractions are hardly used in these applications because of their tendency to disintegrate under thermal treatment because of the metallic impurities. The coarse fractions of BSA 96 such as 5–8 mm and 6–15 mm were successfully used to improve thermal shock resistance of pre-cast shapes.

Another idea was to modify the thermo-mechanical properties of an alumina spinel castable by inclusion of small additions of BSA 96. However at sintering temperatures of 1400 °C the test recipes showed some abnormal linear expansion of up to 3 %.

4.5 CAM phase formation in BSA 96 based cement bonded spinel containing castables

In order to find the root cause for such an expansion, different test castables were investigated. The outcome was that the expansion would only happen when BSA 96

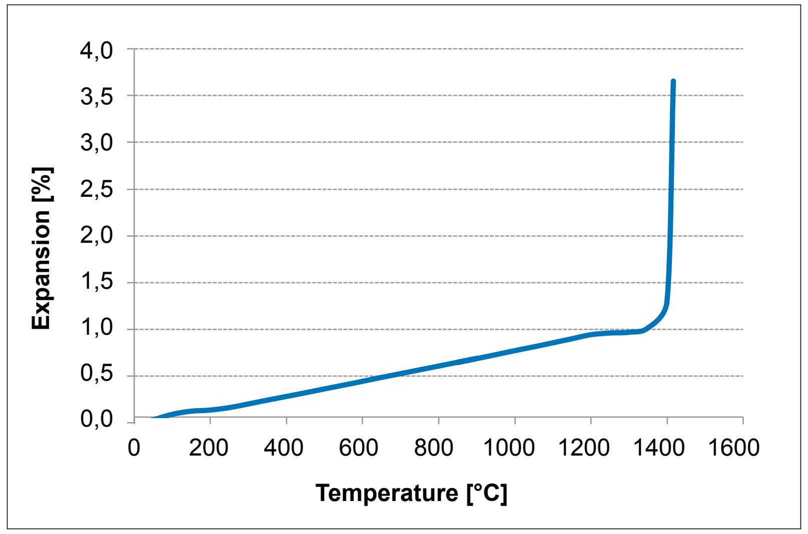

Fig. 8 Dilatometer measurement of dry test mixture containing 40 mass-% BSA 96 <90 µm, 40 mass-% AR 78 <45 µm and 20 mass-% CA-270

is used in fines of the matrix compound in combination with fine spinel and cement as binder.

Fig. 8 shows the dilatometry curve of a dry mixture containing 40 mass-% BSA 96 <90 µm, 40 mass-% spinel AR 78 <45 µm and 20 mass-% cement CA-270. The curve shows a very strong expansion reaction at temperatures above 1350 °C and confirms previous PLC measurements of test castables.

Mineralogical investigations were performed to further understand the reactions leading to expansion. Fig. 9 shows the SEM image measured with backscattered electrons (BSE) of the same mixture as for the dilatometer investigations but sintered at 1400 °C for 5 h in a lab furnace. The alumina grains (A) are surrounded by plate-shaped sinter products. Some of the alumina grains are incorporated by the plates and in some cases broken apart.

Wavelength dispersive X-ray (WDX) measurements have shown that the chemical composition of the sinter product is close to the CAM-I phase ($C_2M_2A_{14}$) as reported by Göbbels et al., which is near to the structure of CA_6. [8]

In an impurity-free system such as typical alumina spinel castables, the CAM phases are expected to be formed at a temperature range of 1600–1650 °C. At such elevated temperatures the sinter densification is expected to compensate the expansion reaction. With BSA 96 the CAM phases are formed at lower temperatures. It is assumed

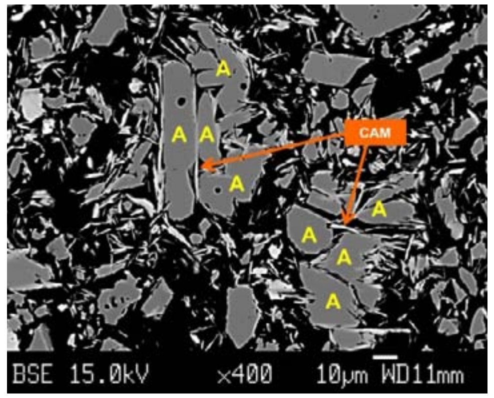

Fig. 9 BSE image of fired test mixture containing BSA 96, spinel and CAC

that this is due to slight melt formation at the grain boundaries. The presence of such a thin film of melt is enough to increase the ion mobility and to accelerate the formation of CAM phases at temperatures below where any sinter densification could compensate expansion.

5 Summary

In 2011 Almatis introduced BSA 96 as alternative European high alumina aggregate. Since its launch many customers have tested it and changed their recipes to include BSA 96. The new sintered aggregate is now found in a wide field of applications such as high alumina bricks, alumina magnesia carbon (AMC) bricks and monolithics.

In AMC bricks BSA 96 shows an earlier and a more even spinel formation when compared to fused aggregates. To reduce excessive expansion of the refractory materials, slight modifications, especially in the matrix, are sufficient to lower expansion reactions to a level similar to that observed with fused aggregates.

Spinel containing high alumina castables, doped with BSA 96 fines in the matrix showed some strong expansion. More in depth investigations showed that this expansion is caused by the formation of CAM phases, but can only occur when spinel, BSA 96 and cement are used together as matrix components.

In the formulation for blast furnace runners it was noticed, that the replacement of BFA by BSA 96 may require an adjustment of the cement and Al-reaction. On site, BSA 96 based castables showed at least similar corrosion resistance to BFA based mixes. This can be attributed to the very small mean pore diameter of BSA 96 of only 0,38 µm. The lower bulk density of BSA 96 when compared to brown fused alumina reduces the specific material consumption therefore providing an economic advantage in the range of 3–5 %.

Customers confirmed the reliable performance of BSA 96 in the formulation and processing of their refractory materials, for example giving good flow and reliable setting behaviour in refractory castables and providing smooth brick production.

More tests are on-going in tap hole clays, phosphate bonded mortars and ramming mixes, and also in various castable formulations for pre-shape production and also in special gunning applications.

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