NEW EUROPEAN SINTER AGGREGATE WITH 96 % AL_2O_3

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ABSTRACT

The market situation for high alumina aggregates from China has changed considerably over the past five years. Not only the availability and pricing but also the quality has become an issue for European refractory producers. A new aggregate with 96 % Al_2O_3 has been developed and made in Europe and which is independent from Chinese raw materials. It is produced by a sinter process and provides the same homogeneous product properties which are well known for other established sintered aggregates such as tabular alumina and sintered spinel. This paper presents the properties of the new refractory aggregate and laboratory results of refractories based on it. The new aggregate provides an alternative to other high alumina aggregates, fused, natural, and sintered. First industrial application trials are on-going.

INTRODUCTION

Many changes have taken place in the refractory world over the past 20 years. In the 1990s, low priced bauxite from China replaced other alumina materials such as andalusite, mullite, and in some cases even chamotte based materials. The general perception that higher alumina content meant higher performance made it relatively easy for the refractory producers to sell new refractories with higher alumina content. In that time the global refractory industry became very dependent upon Chinese bauxite and brown fused alumina.

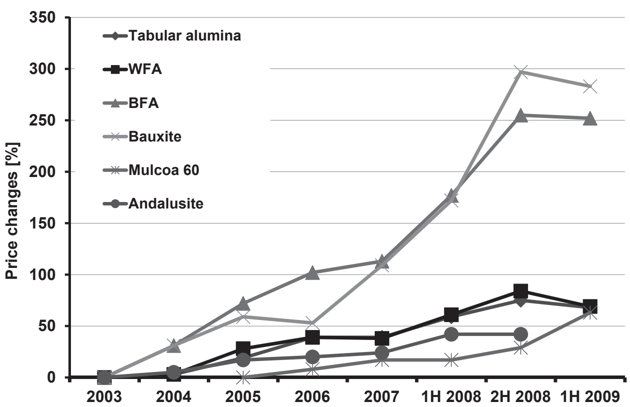


Fig. 1: Price development of high alumina refractory raw materials 2003 – 2009 [1]

The situation has changed dramatically in the past few years and especially since 2007. The tremendous growth of steel production in China significantly increased the internal demand for refractories and raw materials. The Chinese policy has changed from supporting raw material export to discouraging it [2]. Bauxite and brown fused alumina exports from China have been limited in volume by export licences and are now subject to taxes and fees. This has resulted in steep price increases in the world market (**Figure 1**).

The world economic crisis in 2009 has only temporarily eased the situation. The global refractory industry is now challenged to establish alternatives both from availability and also from a strategic point of view. The new high alumina material BSA 96, which is made in Europe and is independent from Chinese raw materials, provides an alternative to imported high alumina aggregates – fused or natural. This paper describes the properties of the latest aggregate in the Almatis product portfolio. It will also present a brief overview of the special characteristics of BSA 96 in various formulations in comparison with other high alumina aggregates.

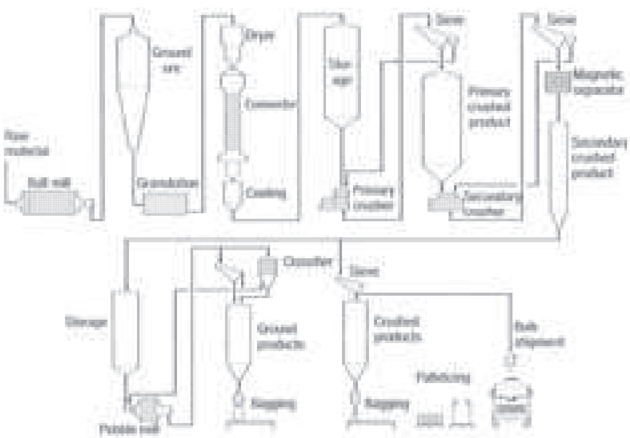


Fig. 2: Production process of ALMATIS sintered aggregates

MANUFACTURING OF BSA 96

The manufacturing of fired high-alumina aggregates generally requires 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 itself is a very energy intensive process, requiring 2,000 kWh of electricity per tonne of product [3,4]. 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 manufacture of BSA 96 is identical to the production of tabular alumina and sintered spinels, which is described in detail by MacZura [5] (**Figure 2**). The alumina feedstock is ground and agglomerated in a granulation process into a ball of typically 25-30 mm in diameter. After transportation to a drying chamber the moisture of the compacted green balls is removed prior to being transferred to the top of the shaft kiln (Curtis converter). The dried balls are sintered in a continuous vertical shaft kiln thereby converting to BSA 96 at temperatures of 1700 to 1800 °C. The kiln is operated by combustion of a mixture of natural gas and air.

The sintered balls are cooled, crushed and screened to produce graded aggregates. Intensive magnetic de-ironing is incorporated

into the process to remove iron contamination in the final products. The 90 µm powder is produced by grinding BSA 96 grains in a ceramic-lined ball mill with ceramic grinding media.
Sintering temperature, heating and cooling rates are important criteria for the quality of the sintered BSA 96 and are therefore strictly controlled. Frequent in-process samples are taken for control of parameters such as the microstructure of the fired balls to guarantee a stable product quality. Further quality control is carried out by the laboratory, monitoring both the chemical composition and the physical properties of the material. These are bulk specific gravity, apparent porosity and water absorption. BSA96 is available in various closed and open grain sizes. Closed sizes: 6-15 mm, 5-8 mm, 1-3 mm, 0.5-1 mm; open sizes: 0-1 mm, 0-0.5 mm, and -90 µm.

FEATURES OF FUSED AND SINTERED AGGRE-GATES

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.
Brown fused alumina is made by fusing pre-calcined non-metallurgical bauxite in a batch or semi-batch furnace [3]. 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. Unless the fusion process is carefully controlled, the product may contain residual carbides and other impurities. Furthermore the cooling procedure of a fused material is an important quality criterion for this type of aggregate. It is often stated that fused grains would show a better chemical resistance when compared to sintered aggregates due to their large crystal size of several hundred microns. The formation of these large crystals requires a slow cooling process to allow crystal growth. Nowadays, for economic reasons, this highly important cooling is often forced and as a consequence the quality of the fused aggregates deteriorates. Small crystals and a high open porosity, sometimes even up to 10 % are the consequence.
A shortened fusion process and accelerated cooling increases the amount of residual carbides and/or metallic components in the fused product. Because of to the temperature gradient within a fused block, different zones form during the solidification and crystallisation process. This requires a careful selection after crushing of the fused block into chunks.
In general it can be stated that brown fused alumina is a much more inhomogeneous product when compared to the sintered aggregate BSA 96. 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. No carbides or metallic components at all are formed during the sintering process.

MATERIAL PROPERTIES OF BSA 96

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 (**Table 2**). The bulk density of BSA 96 is lower when compared to brown fused alumina. This is a typical feature of sintered aggregates due to the small closed pores in the microstructure. The open porosity is the same or even lower when compared to fused aggregates.

Chemical Composition

BSA 96 is a refractory aggregate with an Al_2O_3 content greater than 96 %. The major impurities are SiO_2 and TiO_2 and smaller amounts of Na_2O and MgO (**Table 1**). It is important to mention that because BSA 96 is produced by the sinter process all size fractions have the same chemical composition. Even the fine milled BSA 96 -90 µm has the same chemical composition as the coarser fractions (**Table 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 introduced during the crushing and sizing of the fractions. As a consequence BSA 96 does not contain carbides or metallic components that could do harm to sensitive bonding systems. This is different to fused aggregates where impurities often accumulate in the fine fractions. These impurities may react with water and deteriorate the flow and 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.

Tab. 1: Physical and chemical properties of BSA 96

Chemical Composition		typical
Al_2O_3	[%]	96.5
TiO_2	[%]	1.2
SiO_2	[%]	0.9
MgO	[%]	0.3
Na_2O	[%]	0.3
Fe_2O_3	[%]	0.15
Physical Properties		**typical**
Bulk Specific Gravity	[g/cm³]	3.5
Apparent Porosity	[%]	4.5
Water absorption	[%]	1.3

Tab. 2: Chemical composition of BSA 96 fractions

	6-15	3-6	1-3	0,5-1	
Na_2O	0.30	0.32	0.31	0.31	0.29
Fe_2O_3	0.15	0.14	0.15	0.15	0.15
SiO_2	0.91	1.10	1.06	1.04	0.95

Microstructure and Phase Composition

The major phase of the BSA 96 aggregate is corundum with a minor amount of tialite (Al_2TiO_5). **Figure 3** shows the typical corundum crystals with entrapped porosity. This explains the reduced bulk density of this sintered aggregate when compared to a fused aggregate such as brown fused alumina.

BSA 96 REFRACTORY PROPERTIES

Different castable and refractory brick formulations have been tested to demonstrate the performance of BSA 96 aggregate in comparison to other high alumina raw materials.

High purity low cement castable

Classical physical properties for castables such as water demand, flow, and strength development were tested in a low cement (LC) vibration castable and compared to a castable based on a premium grade brown fused alumina (BFA) (**Table 3**).
E-SY 1000 was used as the matrix alumina and the percentage of the aggregate fractions was adjusted to meet the same particle size distribution. It is clear, that because of the density differences between the sintered and the fused aggregates, a simple 1:1 ex-

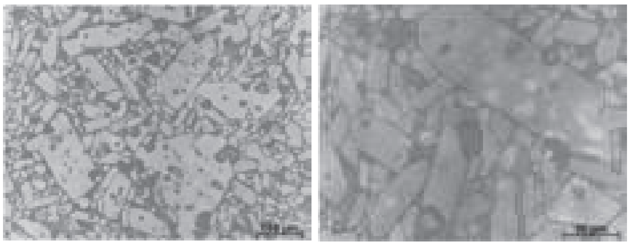


Fig. 3: SEM micrographs of BSA 96 grain; thermally etched at 1500°C

Tab. 3: LC-castable formulation

LC-CASTABLE based on			BSA 96	BFA
Aggregates	3 – 6 mm	%	25	30
	1 – 3 mm	%	20	20
	0.5 – 1 mm	%	10	15
	0 – 0.5 mm	%	20	10
	0 – 0.3 mm	%	-	5*
Alumina	E-SY 1000	%	20	15
Cement	CA-14 M	%	5	5
Additives	ADS 3 / ADW 1	%	1.0	1.0
*Addition of 5% Tabular alumina T60/T64 to match desired particle size dis				

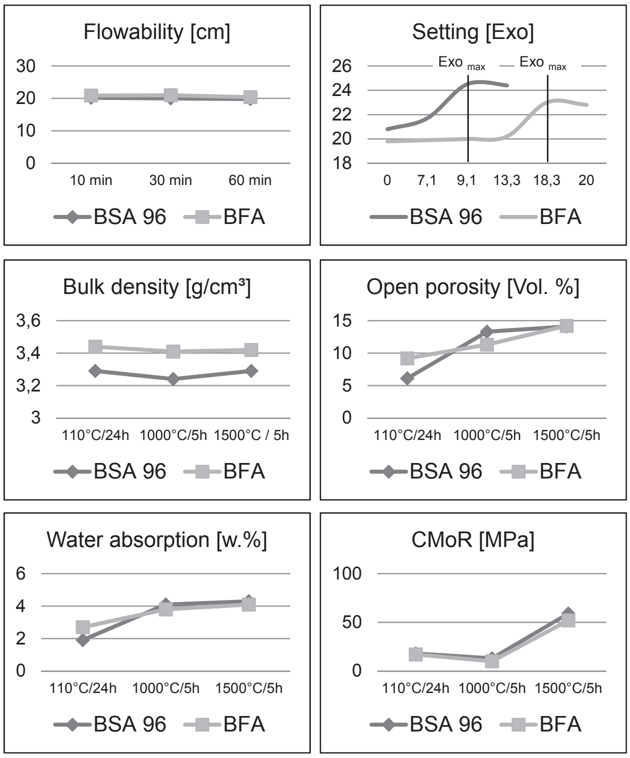


Fig. 4: Comparison of physical properties of BSA 96- and BFA-based LC-castables

change of the weight fractions is not possible in order to achieve the same particle size distribution of the castable. Such recipe adjustment will almost always be required when a fused aggregate is replaced by a sintered aggregate in a refractory formulation.

The working time was adjusted to >2 h by dispersing alumina ADS 3 and ADW 1. All tests were performed according to EN 1402.

The physical properties of the test castables are shown in **figure 4**. Both castables show a very similar flow profile with the same amount of mixing water (4.0 %). Although the same ratio of ADS 3/ADW 1 was used for both formulations, the setting of the castable based on BFA was significantly delayed. With an EXO_{max} measurement of 18 h it took twice the time for the BFA based castable to reach its final set when compared to the BSA 96 version which had achieved an EXO_{max} after 9 h. It is assumed that the retarded set of the brown fused alumina formulation is caused by the impurity levels of the fused aggregate.

The strength values after drying and firing are similar for both formulations. The bulk density of the castable based on BSA 96 is 6-8 % lower when compared to BFA. However, the water absorption and open porosity are comparable. This proves that the lower density is only due to the higher amount of closed pores in the sintered BSA 96 and will not negatively influence the corrosion resistance of the formulation. The refractoriness under load (0.2 MPa) of the BSA 96 castable (pre-fired at 1000°C) shows a maximum expansion of 0.98% at 1350 °C, a T_1 of 1626 °C, and a T_5 of >1700 °C.

BSA96 in castables for blast furnace runners

Low cement and ultra-low cement castables with 60-85 % Al_2O_3 and 5-25 % SiC are used for the wear lining in the main trough. Brown fused alumina is the most common aggregate for these castables although tabular alumina is also used in some cases [6]. The BFA price increases and various quality issues have led to increased interest in alternative high alumina aggregates for this application. Industrial tests with BSA 96 are on-going.

Table 4 shows a comparison between a BSA 96 and a BFA based ultra-low cement (ULC) vibration castable. The matrix composition has been kept constant, and only the aggregate fraction has been exchanged.

Both castables show comparable strength data and a similar oxidation behaviour. The higher density of the BFA aggregate (3.8 g/cm³) when compared to BSA 96 (3.50 g/cm³) shows in a 3 to 4 % higher density of the castable. The material demand for a lining is therefore 3 to 4 % lower when BSA 96 is used as the aggregate.

Tab. 4: Comparison of BSA 96 and BFA containing castable for blast furnace runners ("black castable")

ULC-CASTABLE based on			BSA 96	BFA
Aggregates	1 – 10 mm	%	50	50
	0 – 1 mm	%	-	7
	0.5 – 1 mm	%	4	-
	0 – 0.5 mm	%	3	-
SiC	0 – 1 mm	%	20	20
Alumina	E-SY 1000	%	15.2	15.2
Cement	CA-270	%	2	2
Carbon - Additives		%	5,8	5,8
Dispersing Additives		%	+0,12	+0,12
H_2O		%	4.5	4.5
Density	110°C/24h	g/cm³	2,96	3,06
	1000°C /5h	g/cm³	2,90	3,02
Open porosity	110°C/24h	Vol.%	12.0	11.4
	1000°C /5h	Vol.%	19.0	19.2
CCS	110°C/24h	MPa	65	54
	1000°C /5h	MPa	64	55
PLC	110°C/24h	%	-0.05	-0.02
	1000°C /5h	%	+0.76	+1,17
Physical properties determined after firing in oxidizing atmosphere				

AluMagCarbon bricks based on BSA 96

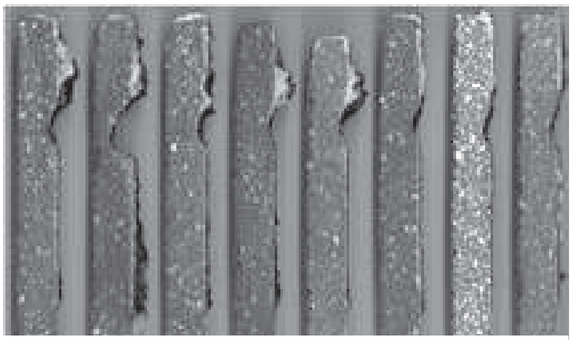
The typical raw materials used for AluMagCarbon (AMC) bricks are bauxite or brown fused alumina. For high areas of high demand, such as the impact pad in steel ladles, AMC bricks based on high purity raw materials such as tabular alumina proved to per-form best. Apart from the corrosion resistance, the spinel formation rate and amount of formed spinel are important factors for the final performance.

The slag resistance of an AMC brick based on BSA 96 was determined in comparison to AMC bricks with an identical matrix but based on different high alumina aggregates: white fused alumina (WFA), tabular alumina (TAB), BFA, bauxite (BX) and a commercially available brick containing a mixture of white and brown fused alumina (WBFA) (**Table 5**).

Tab. 5: Properties of tested AMC bricks

Chemical composition							
		WFA	TAB	BFA	BX	BSA-96	WBFA
Al_2O_3	%	91,9	90,7	86,0	78,1	88,9	88,7
SiO_2	%	0,19	0,22	0,90	6,82	1,05	0,90
Fe_2O_3	%	0,13	0,16	0,23	1,68	0,25	0,26
Na_2O	%	0,22	0,26	0,04	0,06	0,28	0,20
MgO	%	7,44	8,49	9,51	8,91	7,77	8,86
C	%	7,16	7,47	8,63	8,30	6,60	6,98
Tempered							
Bulk density	g/cm³	3,23	3,15	3,28	2,95	3,17	3,28
o. Porosity	Vol.%	4,0	2,3	2,2	4,8	3,4	5,0
Red.1000°C 5 h							
Bulk density	g/cm³	3,19	3,12	3,26	2,91	3,14	3,22
o. Porosity	Vol.%	12,9	10,9	10,9	13,9	10,9	11,2

The test was conducted in an induction furnace at the German Refractory Institute (DIFK)/Bonn. The samples were simultaneously subjected to 15 kg of steel ST 52 under oxidising atmosphere (air). 750 g of calcium aluminate slag ($CaO:Al_2O_3$ = 1.08) with the following composition (in weight %) 40 CaO / 37 Al_2O_3 / 5 SiO_2 / 5 MgO / 3 FeO / 4 MnO, and 6 CaF_2 was added after reaching the test temperature of 1650°C. The test was aborted after only 1 h because of the high wear of the BX based AMC brick. The test specimens were cut in a longitudinal direction and the wear profile measured at the slag level. The discoloration of the sample, slag penetration, and the formation of cracks were also studied.



	WBFA	BX	WBFA	BFA	BSA 96	WFA	TAB	BSA 96
mm/h	5,4	14,6	5,5	4,4	5,2	4,4	5,0	5,5

Fig. 5: Cut sections of AMC bricks after induction furnace test at 1650 °C and average wear rate at slag level in mm/h.

Figure 5 illustrates the result of the corrosion test on the cut samples. The bauxite based AMC brick shows by far the highest wear. The corrosion speed of the BSA 96 brick was 5.3 mm/h on average and is at a comparable level to the other high alumina aggregates in the test.

CO-resistance of fired BSA 96 bricks

Various industrial processes operate under carbon monoxide (CO) conditions. Only CO-resistant refractory raw materials are suitable aggregates for the formulation of dense castables or bricks to be used in such an environment. Iron or iron oxide contamination in refractory raw materials destroys the CO resistance. A new 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 hours. The BSA 96 brick was rated class A (best achievable) [7].

SUMMARY

The new high alumina sintered aggregate BSA 96 is produced by Almatis in Ludwigshafen, Germany and is independent from Chinese raw materials. It provides a technical and strategic alternative to Chinese brown fused alumina and refractory bauxite. BSA 96 is a homogeneous sintered product with the same chemical composition across all size fractions. It is free of carbide or metallic contaminants which can disturb the performance of fused high alumina aggregates in monolithic and brick applications. A sintered aggregate such as BSA 96 provides reliable performance in the formulation and processing of refractory materials, for example giving good flow and setting behaviour in refractory castables. BSA 96 has intra-granular closed porosity similar to tabular alumina and therefore the bulk density is 5 to 8 % lower when compared to brown fused alumina. The open porosity, which is important for the corrosion resistance, is in the same range or lower. Because of the difference in bulk density between sintered and fused aggregate, normally recipe adjustments will be needed when replacing a fused by a sintered aggregate in a refractory formulation.

Lower density aggregates provide an economic advantage by lower material consumption. The density difference between fused and sintered aggregates in the range of 5 to 8 % should be considered when an economic comparison is made between both concepts.

Industrial trials in blast furnace runners and brick applications are on-going, and in some cases BSA 96 has already replaced brown fused alumina.

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