Review of Tabular Alumina as High Performance Refractory Material

G. Büchel, X. Liu, A. Buhr, J. Dutton

Dr. Gunter Büchel is Manager R&D Refractories, Ceramics, Polishing and Market Development Europe at Almatis GmbH (Frankfurt, Germany). Between 1998 and 1996 he studied Chemistry at the Johannes-Gutenberg University Mainz (Germany) and the University of Padova (Italy). In 1993 he earned his PhD in Chemistry from the Johannes-Gutenberg University. Afterwards carrying out postdoctoral studies at the CNRS Marseille (France). From 2000 to 2001 he was scientific employee at the Advanced Ceramics Group of the Technical University Hamburg-Harburg (Germany). Since July 2001 he has been in charge of Almatis GmbH (previously Alcoa World Chemicals) in various positions: as Application and Market Development Manager, Process Engineer, and currently as Manager R&D and application support for customers in Germany, Central- and East Europe.

Dr. Andreas Buhr is Global Technical Director Refractories, Ceramics, Polishing at Almatis GmbH (Frankfurt, Germany). He studied Mineralogy at the universities in Bonn and Aachen and received his PhD at RWTH Aachen in 1996. Between 1996 and 1998 he was employed at Thyssen Krupp Stahl AG (Dortmund, Germany) as head of the refractories laboratory. Since 1998 he is with Almatis (previously Alcoa World Chemicals) in Frankfurt.

Xinyu Liu is Technical Manager Asia at Qingdao Almatis Co., Ltd. (Qingdao / China). From 1981 till 1985 he studied at the Hunan University, earning his B.Sc. on Ceramic Science and Engineering. From 1985 till 1988 he was postgraduate at Luoyang Institute of Refractories Research, earning his M.Sc. on nonmetallic inorganic materials. 1988-1997 he was with Luoyang Institute of Refractories Research as Deputy Manager for R&D and Market Development. Since July 1997 he is employed by Qingdao Almatis Co., Ltd. (previously Alcoa Industrial Chemicals) as Technical Manager in charge of market development and application support for Asia.

Jerry Dutton was with Almatis UK Ltd. as Regional Account Manager and has retired since June 2007. He was graduated B.Sc. in Metallurgy from Manchester University, and had joined Alcoa in 1974, since 2004 Almatis UK Ltd.

1 Introduction

For more than 70 years tabular alumina has been widely used in high performance refractory materials for many applications in steel, foundries, petrochemistry, and ceramics. Its superior refractoriness, thermal shock resistance, creep resistance and abrasion resistance has made tabular alumina the dominant synthetic high purity Al₂O₃ aggregate. Despite the fact that the overall consumption of refractories has seen a tremendous decline e.g. in steel production, the use of tabular alumina has grown relatively and in absolute terms. Beside the sintered tabular alumina white fused alumina is also being used in many refractory applications. The purpose of this review paper is to describe and compare the specific properties of tabular alumina and white fused alumina and to discuss advantages of tabular alumina in various applications.

2 Synthetic alumina aggregates

2.1 Tabular alumina production process

Tabular alumina was produced for the first time in 1934 by Thomas S. Curtis under Alcoa contract using his patented shaft furnace. The name tabular alumina is derived from large, typically 50-400 μm flat tablet-like synthetic corundum (α-alumina) crystals, which are visible in fractured surfaces of tabular alumina.

The production process (Fig. 1) starts with the grinding of a purified synthetic calcined alumina from the Bayer process, which then is agglomerated in a granulation process. In the special Almatis ball-forming process, green balls are made only with water and without the use of any additives, e.g. organic binders or TiO₂. 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 (converter). The dried green balls are sintered in a continuous vertical shaft kiln thereby converting to tabular alumina at temperatures of 1600-1900°C. The kiln is fired by a combination of natural gas and air.
2.2 Tabular alumina properties

Tabular alumina is a homogeneously sintered dense aggregate with a high melting point of 2050 °C. Main chemical impurities are Na₂O from the Bayer alumina, and metallic iron from the different crushing steps. Due to the continuous sintering process, the Na₂O content is homogeneously distributed through the whole product range without any portions containing much higher impurity levels. Metallic iron is carefully removed by passing the crushed products over several magnetic drums.

No additives are added to Almatis tabular alumina. Potential additives could be organic binders to facilitate the ball forming process, or TiO₂ to lower the sintering temperature during conversion. Those additives would negatively influence tabular alumina properties, e.g., the consistency of the crystal structure, the open porosity or the hot properties. High densification could be achieved with TiO₂ addition [2], but liquid-phase sintering would already appear at 1350 °C with Bayer alumina (Na₂O 0.4–0.5%) [3].

The main physical characteristics of tabular alumina are bulk specific gravity (BSG), apparent porosity (AP) and water absorption (WA) (Table 1). Properly fired tabular alumina has α-alumina crystals that can easily be seen in reflected light by the naked eye. The appearance of these crystals can be compared with acceptability standards by visual inspection of the fractured surfaces. The structure of tabular alumina with large corundum crystals has no visual open pores and has low open porosity of typically only 2.9%.

The microstructure as shown in Fig. 2a reveals that tabular alumina has only small pores, either closed or interfacial, and these pores are evenly distributed into the whole structure. This contributes to the low water absorption.

The high amount of closed spherical porosity of less than 10 μm in diameter can also be seen in Fig. 3. Careful control of firing during production is required since under- and over-fired tabular alumina exhibits a high amount of open porosity which reduces BSG and increases water absorption of both tabular alumina and the final refractory products. An excessive
open porosity would also result in greatly differing grain strength and high-temperature volume stability. Partially sintered grains would exhibit poor volume stability and shrink further when used in fired refractories. The resulting defect structure would lead to a weakness of the refractory and is a source of high porosity which limits corrosion/erosion resistance of the refractory in service. Sintering aids could overcome these low densities, but, besides inferior hot properties, crystal growth is limited resulting in lower thermal shock resistance [1].

Because of the amount of closed porosity in tabular alumina the thermal spalling resistance (TSR) is very high (Fig. 4). The spherical closed pores react to thermal shock as a crack stopper. They avoid further propagation of the crack through the whole grain. The result is a high crushing strength of the individual grains and of the whole refractory castable or brick formulation even after thermal shock.

### 2.3 The global tabular product concept of Almatis

Almatis as a global supplier of premium alumina raw materials supports customers in the refractory industry to enhance their business in a more and more global business environment.

Tabular alumina T69/T64 is one product. Historically, the name T69 was used in all countries except North America, and T64 was used for the North American market. Therefore, for the global tabular products the name T69/T64 is used.

Since 2001, 14 standard grades have been offered as Global Products (Table 2). Additional special regional grades are available on request.

The chemical specification was harmonised in 2001.

The particle size distribution is specified in millimetres and Tyler mesh, with equivalent sieves across the whole particle size distribution. Also, the test methods and the information provided on the Certificate of Analysis (CoA) have been harmonised for the tabular products.

Tabular alumina T69/T64 is globally available from five plants (Rotterdam/The Netherlands; Ludwigshafen/Germany; Lectsdaile/North America; Palia/India; Qingdao/China) to the same specifications.

In the meantime, the global tabular product concept has proved its value in the global market. The technology transfer processes of our customers have become much easier, because formulations do not need to be adjusted with regard to particle size distribution. If global tabular sizes are used. Also resources and time consuming additional testing and qualification of finished products by the end-user can be reduced or even avoided.

T69 is a regional tabular alumina produced at Iwakuni (Japan). It has a lower Na₂O content compared to standard T69/T64 (max. 0.2% vs. 0.4%) and a higher bulk specific gravity compared to standard T69/T64 (typically 3.7 vs. 3.55 g/cm³). The sizes are not specifically harmonised with the global tabular products, although the particle size distribution for most of the sizes is similar to T69/T64 global products.

### 2.4 White fused alumina production process

Fused alumina was first produced in the late 19th century by fusing an alumina feedstock in a batch process with carbon electrodes and subsequent cooling [4]. Depending on the type and amount of impurities in the feedstock, fused alumina is available as brown-, white-, pink-, ruby-, and black fused alumina.

White fused alumina (WFA) is produced by a batch melting process of a Bayer alumina feedstock. After melting of white fused alumina, primary cooling of the block takes place and Na₂O is segregated in the upper central portion of the fused block as β-alumina (Na₂O·11Al₂O₃). Secondary cooling begins after block is dumped onto a bed of alumina fines. Due to the inherent cooling of the molten alumina block, WFA properties differ between the inner and the outer part of the WFA block. Besides the difference in Na₂O
content, the crystal size and the open porosity also vary in the different regions. After cooling, the block is broken into chunks < 40 mm by dropping a large steel ball onto it. Careful selection of the various WFA grades is required to separate the low-purity WFA and the small crystal size fused alumina from the higher quality portion. The selected chunks are crushed and subsequently screened and passed over a magnetic separator.

### 2.5 White fused alumina properties

Dependent on the purity of the feedstock and on the selection of the various fused alumina grades within a fused alumina block, different grades of fused alumina are available. In the outer part of the fused alumina block cooling proceeds much faster resulting in smaller corundum crystals, whereas in the inner central part cooling is slow and crystals can grow up to large single crystals. These crystals usually already contain micro cracks induced during crushing. These reduce the crushing strength of the single grains.

Na$_2$O is the impurity which most affects the properties of WFA. The total Na$_2$O content of a fused alumina block is not higher than that of tabular alumina. However, due to the batch production process of fused alumina, the Na$_2$O is not homogeneously distributed within the fused alumina block as it is in tabular CD. There are certain areas with very low, and other with very high Na$_2$O content. The Na$_2$O content at different locations in white fused alumina blocks varies between 0.07% and 4.0% [41]. Careful selection is therefore required after the first crushing of the fused alumina block into chunks. In a large block, the Na$_2$O can be partially removed by discarding the top centre section.

When compared to fused alumina, the continuous sintering process of tabular alumina gives a constant Na$_2$O level over the whole production range, so no selection is required.

The Na$_2$O forms β-alumina (Na$_2$O·11Al$_2$O$_3$) by reaction with Al$_2$O$_3$. The Mohs hardness of β-alumina is much lower when compared to corundum (6.5-7 vs. 9). Subsequently during crushing and sieving the low-hardness β-alumina powders into smaller sizes than corundum resulting in an accumulation of Na$_2$O in the WFA fines (segregation). In particular the WFA fines below 45 μm carry a significant amount of soluble Na$_2$O which has a significant impact on castable setting behaviour and refractoriness. One author reports that the soda content increases from 0.31% in coarse sizes (> 14 mesh) to 1.08% in the fines (< 120 mesh) [4].

The influence of soluble Na$_2$O on the flow behaviour of low cement castables is well known and was confirmed by own experiments. Table 3 shows a comparison of two tabular alumina castables, where only 7% of the tabular alumina -20 μm fines have been exchanged for 7% white fused alumina dust -20 μm. To achieve the same flow, the castable with white fused alumina requires 5.3% water instead of only 4.7% with tabular alumina -20 μm.

![Fig. 5a](image1.png)  
**Fig. 5a** Visual appearance of tabular alumina and white fused alumina

![Fig. 5b](image2.png)  
**Fig. 5b** Visual appearance of tabular alumina (a) and white fused alumina (b)

### 3 Application of tabular alumina and white fused alumina

The main volume market for refractory aggregates such as tabular alumina and white fused alumina is the refractory industry, where these aggregates are used in combination with spinel, calcined and reactive alumina, and binders such as calcium aluminate cement, clay or resin. The total global tabular and white fused alumina
consumption is estimated at 620,000 t, split by region – Europe around 220,000 t, Americas 140,000 t and Asia 270,000 t. Refractory applications for high-purity alumina raw materials are the iron and steel making industry, foundries, aluminium investment casting, and the petrochemical and ceramic industries. About 65-70% of refractories are used as monolithics or bricks in the iron and steel industry. The continuous advancement of steeldmaking technology and processes requires higher quality refractories which, despite an overall decrease in specific refractory consumption in steelmaking, results in an increased use of synthetic alumina raw materials [5]. It is estimated that more than 80% of the total tabular alumina and white fused alumina volume in refractories is consumed by the iron and steel industry.

Key advantages of tabular alumina are high thermal mechanical strength, chemical stability, high thermal shock resistance, high abrasion resistance, and consistent properties. Tabular alumina provides reliable performance and avoids adjustments to overcome quality variations of the refractory aggregate. In contrast to tabular alumina, the use of white fused alumina appears to be more sensitive and the way of which formulations are prepared should be different. Some studies show that to achieve a certain vibration flow of say 20 cm, the water demand increases from approx. 8.3% to approx. 10.3% by exchanging only one tabular alumina size for the corresponding white fused alumina size [7]. A 2% higher water demand results in a 6% higher open porosity of the fired castable, which significantly reduces the infiltration resistance.

### 3.1 Sliding gate plates

The first successful application of tabular alumina was the sliding gate plate, where the thermal shock and wear resistance was clearly improved. The use of tabular alumina in sliding gate plates is state of the art technology worldwide. The development of sliding gate plate refractories has been described by several authors [8–12]. Commonly used Mullite-bonded alumina refractories (80–90% Al₂O₃) have been improved by reducing silica content and adding graphite and also by carbon bonding. Mullite further improves the thermal shock resistance but its SiO₂ content decreases the resistance against corrosion caused by calcium-treated steel. High manganese steel, and high oxygen steel. Slag gate plates with an addition of ZrO₂ instead of SiO₂ demonstrate high corrosion and high thermal shock resistance. The specific refractory consumption of sliding gate plates is around 0.05 kg/t of steel.

#### 3.2 Castables in steel ladle side wall and bottom

The increasing demand for steel cleanliness and the continuous casting technology requires a variety of metallurgical processes to be performed in the steel ladle. Details are discussed by Bannenberg [13]. The development of ladle metallurgy has resulted in more severe working conditions for the ladle refractories because of increased tapping temperatures of up to 1750 °C, extended residence time of the steel in the ladle, stirring, heating, and various aggressive slag conditions, for example during desulphurization [14].

Today, basic bricks (magnesia carbon or dolomite) or high alumina castables (tabular alumina, corundum, spinel or spinel-forming) are standard lining materials for steel ladles. They are used either alone or in combination in various installation practices, e.g., alumina-spinel castables at the bottom and in the side wall and magnesia-carbon bricks in the slag line. Ladle lining practices differ significantly between regions and steel plants as a result of different metallurgical processes, working conditions, and refractory concepts. Specific refractory consumption in steel ladles in integrated steelworks is between 1.0–4.0 kg/t of steel and contributes to around 25% of the total refractory consumption in steel production [6].

### 3.3 Pre-cast shapes

The main applications of pre-cast shapes are in steel ladles. Pre-cast shapes are used as purging plugs, injection lances, well blocks, nozzles, impact pads, and pre-cast ladle bottom elements. In the bundling for continuous casting pre-cast shapes are used as clams and weirs to control the steel flow. These refractory products are not only part of the refractory lining but necessary for the performance of a required metallurgical treatment. Temperatures up to 1750 °C in steel ladles require refractory material based upon synthetic alumina raw material such as tabular alumina or spinel. Spinel addition to tabular alumina refractories further increases the performance in respect to thermo-mechanical properties and wear resistance [5]. Alumina-rich spinels such as AR 78 and AR 80 are used for alumina refractories. AR 78 is used predominantly in the fines and AR 80 in coarse sizes. Electric arc furnace delta sections are often made with large pre-cast shapes. The specific refractory consumption of pre-cast shapes in steel manufacturing is around 0.15–0.25 kg/t of steel.

#### 3.4 Fired alumina bricks

High purity corundum brick is widely used as refractory lining for oil cracking units, coal gasifiers, carbon black furnaces, black liquor gasification and other industrial furnaces. The reason is the outstanding performance of corundum brick with respect to chemical corrosion resistance, mechanical abrasion resistance and thermo-mechanical properties like high temperature strength, refractoriness under load and creep resistance, even in environments with corrosive gas or liquid and with high pressure.

Synthetic-alumina based aggregates such as white fused alumina and tabular alumina are the two main aggregates available for high-purity corundum brick. They are selected due to low impurity content (e.g., SiO₂), high bulk density and good thermo-mechanical properties. These properties enable corundum bricks to meet the requirements for thermal, chemical and structural attacks [15] which gasifiers and other furnaces require in operation.

The different processes for WFA and tabular alumina production (fusion vs. sintering) certainly create differences between the aggregate, which also has an impact on the properties and performance of the corundum brick. Tabular alumina is well received and extensively used in refractories for steelmaking such as sliding gate plates, Al₂O₃-MgO-C brick, castables and pre-cast shapes. However, for many years WFA has been commonly used as the aggregate for high-purity fired corundum brick for non-steel applications such as gasifiers and other industrial furnaces. It is often claimed that WFA aggregate has a higher bulk density which consequently increases the density of fired brick and the corrosion resistance which could enhance the overall performance. These perceptions were investigated in an extensive evaluation [16].

High purity corundum brick with Al₂O₃ content above 95% was studied based on tabular alumina and white fused alumina (WFA) as single aggregate and the combination of both. When compared to tabular alumina, WFA aggregate has a higher SiO₂ content of above 0.10% and shows fluctuation on soda content. WFA also has
Table 4 • Brick formulation

<table>
<thead>
<tr>
<th>Aggregate / % (Tabular or WFA)</th>
<th>T100</th>
<th>T75</th>
<th>T50</th>
<th>T25</th>
<th>T0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3 mm</td>
<td>42</td>
<td>19.5+22.5</td>
<td>42</td>
<td>42</td>
<td>40</td>
</tr>
<tr>
<td>0.5-1 mm</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>0-0.5 mm</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Fines / % (Tab -325 mesh or WFA -240 mesh)</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>23</td>
<td>25</td>
</tr>
<tr>
<td>Calcined alumina CT800FG / %</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Sulphite pulp liquor / %</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Amount of Tab / %</td>
<td>100</td>
<td>75</td>
<td>50</td>
<td>25</td>
<td>0</td>
</tr>
</tbody>
</table>

A high open porosity of 8.8%, which very often exists in the form of large single pores or in the form of agglomerations of pores rather than the small closed and evenly distributed pores in tabular alumina. Bricks with different ratios of tabular alumina and WFA were tested for firing shrinkage, bulk density and apparent porosity, cold and hot strength, thermal shock resistance, and abrasion resistance. Slag tests with a coal gasifier slag and an oil cracking slag were also conducted.

Almatis global tabular alumina product T69/64 and a common commercial Chinese WFA grade were selected as the aggregate and fines. In the matrix, Almatis calcined alumina CT800FG was used. Sulphite pulp liquor was used as a temporary binder for corundum-brick making. Five recipes were used in this evaluation (Table 4). The formula is named as T100, T75, T50, T25 and T0 and the numbers stand for tabular alumina content in respective brick. Table 4 gives the details with the tabular alumina content highlighted.

The results of the comprehensive study on tabular alumina and WFA for high purity corundum bricks demonstrate that tabular alumina can generally improve the performance of the bricks and provide more balanced performance. This is summarised as follows:

- Tabular alumina containing bricks show higher sintering reactivity during brick production. This results in improved densification.
- Tabular alumina containing bricks have higher bulk density and lower apparent porosity (Fig. 6).
- Tabular alumina brick has outstanding cold crushing strength and cold modulus of rupture and also the highest hot modulus of rupture at 1500 °C (Fig. 7).
- Tabular alumina brick has the highest abrasion resistance.
- Tabular alumina containing bricks outperform pure WFA-based brick on corrosion and infiltration resistance against slag from coal gasifier and oil cracking unit.
- The co-use of tabular alumina and WFA as aggregates can improve thermal shock resistance of corundum bricks.
- Pure tabular alumina and WFA bricks perform better on creep resistance compared to blends of the aggregates.

3.5 AluMagCarbon bricks & AluCarbon bricks

Compared to other materials such as bauxite, brown fused corundum, or andalusite, synthetic alumina refractory raw materials such as tabular alumina and alumina-rich spinel benefit from very high chemical purity (>99.4 % Al₂O₃, >99.4 % Al₂O₃ + MgO). Refractories based on synthetic materials provide the desired lining life and also thermodynamic stability with respect to steel cleanliness. Corus Ijmuiden reports that the lining life of fired spinel bricks is reduced up to 60% if the SiO₂ content is 1% instead of 0.1% [17].

AluMagCarbon (AMC) bricks consist of alumina aggregate, preferably tabular alumina, fine tabular alumina, ground calcined alumina, magnesium and carbon (graphite and resin binder compounds). During use, AMC bricks expand at the hot face due to spinel formation, which results in reduced wear in the brick joints. The tabular alumina aggregate is used for high refractoriness, thermal shock resistance and cro-
4 Conclusion

Tabular alumina is a superior synthetic alumina aggregate for refractory applications. It
provides a unique combination of important properties such as high refractoriness and hardness, thermal shock resistance, corrosion and abrasion resistance and last but not least very high consistency. This is the result of the specifically designed continuous manufacturing sinter process.

Tabular alumina T60/T64 is offered as a global product to the same specifications from five Alnatis plants worldwide. This standardisation provides benefits to refractory producers in minimising resource consuming qualification work if technology is transferred to other regions in the world. Tabular alumina is a standard refractory aggregate for sliding gate plates, steel ladle refractories, as monolithics or bricks, and precast shapes. The results of the fired corundum bricks made with tabular alumina indicate the future potential in this application, which has up to now mainly white fused alumina.

Tabular alumina was introduced about 70 years ago. Starting with special niche applications such as sliding gate plates it has developed to an important high volume refractory material for demanding applications in the iron and steel and other industries. The demand for tabular alumina is constantly increasing even in mature markets due to technology trends in the end user industry. Alnatis is constantly investing in production capacity to fulfil the needs of a growing global market for reliable high quality and standardised tabular alumina products. In 2006 a newly integrated tabular plant was completed in Qingdao, China to expand existing capacities and a new packaging machine will be invested in the Rotterdam plant to increase the bagging capacity for sized tabular alumina products.