

Review of Matrix Aluminas for Refractory Formulations

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1. Abstract

Historically, ground calcined aluminas were the first high-alumina matrix products that were used in refractory formulations, in both shaped and unshaped products. At that time the flow properties of castables were enhanced by the use of silica fume. This was followed later by the development of fully ground reactive aluminas which contributed to the design of the matrix below 63 μ m. In addition to aggregate fines, a range of bi-modal and multi-modal reactives were also developed. These not only gave improved physical properties but also better castable workability.

This paper reviews matrix alumina developments over time, from basic ground calcines to complex multi-modal matrix products and their globally standardised manufacture.

2. Development of castable technology

In 1983, Clavaud et al [1] described state-of-the-art and historical developments of castable technologies. These can be traced back to the late 1960s. The main driving forces to develop castables were increasing labour cost and the reducing number of skilled bricklayers, as described by Nameishi [2]. The first castable concepts consisted of various aggregate gradings, with the matrix fines below 63 μ m being filled with some fine milled aggregate, but mainly with 15-25% CAC (Calcium Aluminate Cement). Such castable products are classified as CC (Conventional Castable). CCs require mixing water as high as 8-15%, with resultant open porosities of up to 25%. Therefore it was not possible to use these castables in blast furnace runners or steel ladles. They could not replace bricks which were widely used at that time. Bricks show significantly lower porosities, in the range of 15% to 18%, therefore giving better mechanical strength, better slag resistance etc. resulting in a better overall service life. Major innovative work led to the development of LCC

(Low Cement Castable) technology by replacing significant amounts of the CAC with matrix fines (<45 μ m) and submicron fine particles. Such fine products fill the voids between the various coarser matrix fines to further reduce the mixing water demand, resulting in decreased porosity, increased mechanical strength and improved overall performance.

Figure 1 compares the porosity of CC and LCC at various temperatures.

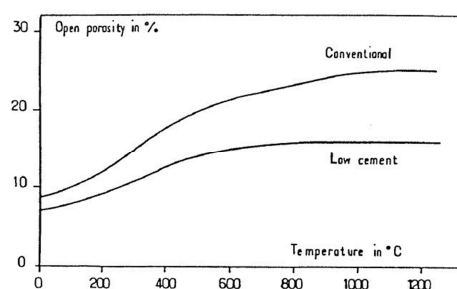


Fig. 1 Open porosity of CC and LCC at various temperatures

The use of matrix fines, initially natural products and more latterly synthetic materials, led to ongoing castable improvements, resulting in the extensive use of monolithics from the early 1990s [2-4].

Typical properties of bricks in comparison to gradually developing monolithic castable products are listed in **table 1**.

Table 1 Typical data of bricks and castables

Material/Properties		Castables			
		Brick	Conventional - 20% CAC	LCC + 5% Silica Fume	LCC - optimised
Al ₂ O ₃	[%]	89	84	90	98
SiO ₂	[%]	9	9	6	-
CaO	[%]	-	5.0	1.5	1.5
Bulk Density 1500°C	[g/cm ³]	2.83	2.80	2.95	3.20
CCS 1500°C	[MPa]	80	95	85	250
HMoR 1500°C	[MPa]	4.5	2.5	< 1	23
Open Porosity >1000°C	[%]	18	26	17	15
Mix. Water - H ₂ O	[%]	-	10	5	4.5

It is clear that only the LCC technology enabled the development of monolithic refractory materials with properties comparable or even superior to bricks.

3. Development of fine matrix filler technology

The obvious failings of CC concepts could only be overcome by the use of naturally available fine particles or the development of synthetic fine fillers for optimised particle packing by filling the voids created by larger fine matrix particles (**Fig.2**).

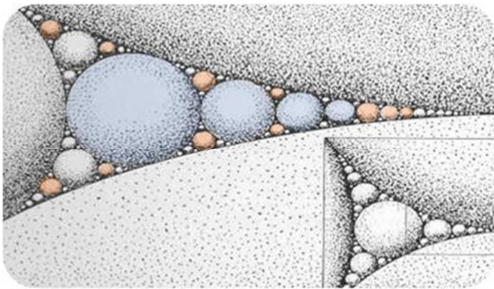


Fig. 2 Particle packing model

These efforts have resulted in reduced water demand, increased mechanical strength, decreased porosity and improved overall performance, allowing reduced cement additions and the development of LCC products with acceptable mechanical strength.

Table 2 lists typical properties and particle sizes of various matrix fine products.

Table 2 Typical properties of matrix fine products

Material / Properties	Al ₂ O ₃ [%]	SiO ₂ [%]	Cr ₂ O ₃ [%]	CaO [%]	BET [m ² /g]	D50 [µm]
Clay	22-27	63-78	-	-	-	2-4
Silica Fume	-	96-98	-	-	15 - 30	0.15
Chromium Oxide	-	-	> 98	-	3 - 10	0.2 - 0.5
Calcium Aluminate Cement CAC 80	80	-	-	20	-	6 - 9
Calcined Alumina general purpose <45µm	> 99.5	-	-	-	0.7 - 1.5	3 - 5
Reactive Alumina submicron	> 99.7	-	-	-	7 - 9	0.5
Reactive Alumina , bi-modal	> 99.7	-	-	-	2.6 - 2.9	2.1 - 2.9

Historically, these were clay, chrome oxide for a limited number of applications and calcium aluminate cement. Also matrix fines from the binder and silica fume were used as submicron matrix filler products. Calcined and reactive aluminas complete the range of matrix fines down to submicron sizes.

One example of matrix fine fillers - the submicron particles of silica fume are shown in **figure 3**.

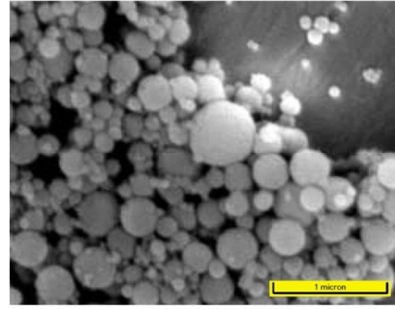


Fig. 3 Silica fume SEM [5]

The very fine matrix filler particles for LCC products require dispersing agents, initially called plasticizers, to reduce the mixing water demand. Common additives such as sodium tri-polyphosphates or, in the later stages of LCC development, poly-acrylates were used for castable dispersion. The use of matrix fines and dispersing agents enabled castables to be used in areas of application where previously, only bricks or ramming mixes could be used.

Silica fume is extensively applied as a submicron filler component in LCCs. Its use has, for example, enabled ramming mixes for blast furnace troughs to be converted into vibration castables, which are easier and quicker to install. However Nameishi [2] stated that the silica level should be decreased for enhanced corrosion resistance.

Silica fume gives significantly reduced hot properties (see HMoR in **Table 1**) due to the formation of viscous anorthite phases at high temperatures in cement-bonded castables [1,6]. This increases progressively with the CaO content (from CAC) in the formulation.

Improvements should be achieved by the development of efficient agents which are able to even further reduce water demand and the use of silica-free matrix fillers.

This led to the important development of castables using calcined and reactive aluminas. Such castables qualify for the use in steel ladles [7-9].

4. Fine alumina matrix filler technology

Initially, it was the ceramic industry that required superfine and fully ground aluminas. Only the use of fully ground products enabled them to achieve the desired sinter reactivity for full densification, >90% of the theoretical density of Al₂O₃ (3.99g/cm³) during firing of advanced ceramics. The term reactive alumina is derived from this sinter reactivity of submicron fine alumina to achieve the required homogeneous microstructures and outstanding mechanical properties. Following on from this, reactive

aluminas with a bi-modal particle size distribution were developed for ceramic slip-casting applications, e.g. alumina crucibles.

Such submicron fines-containing low soda aluminas had already been produced in the 1980s for these ceramic applications, but at relatively low quantities, just to cope with the demand for specialised production of advanced ceramics.

Initially regular ground, medium-crystalline calcined aluminas, milled to 45µm/-325 mesh top size, were used as the fine alumina portion of refractory monolithic castables.

Figure 4 shows the SEM of a ground calcined alumina, clearly showing residual agglomerates of primary alumina crystals showing that the alumina has not been totally ground down to the ultimate primary crystal size.

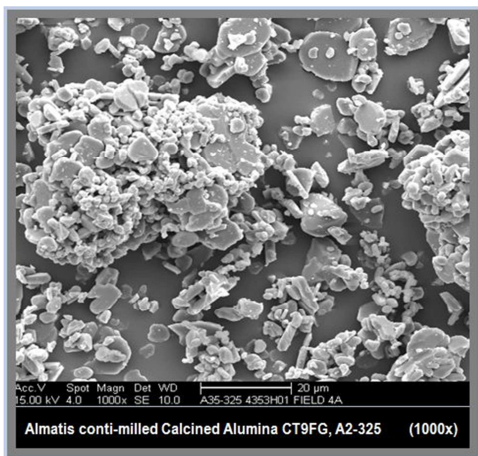


Fig. 4 SEM of ground calcined alumina

Such milled alumina is used as castable matrix fines; however, the residual agglomerates of alumina absorb mixing water which consequently does not contribute to castable dispersion.

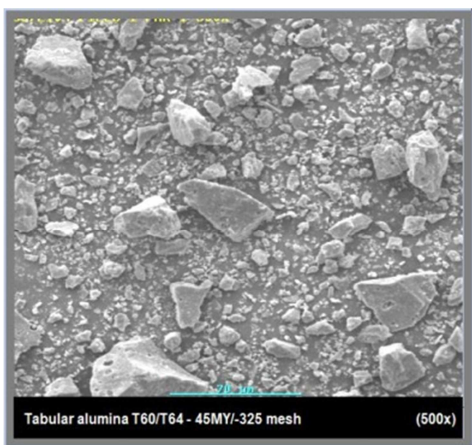


Fig. 5 SEM of Tabular Alumina T-60/T-64 - 45MY/-325 mesh

Agglomerate-free dense matrix fines, e.g. tabular alumina T-60/T-64 -45MY/-325mesh (**Fig.5**), which reduce water demand and improve castable performance, do not show this effect. However, fine tabular alumina <45µm/-325 mesh does not provide sufficient submicron fines to the matrix.

Development took place using the superfine aluminas which had already been produced for advanced ceramic applications, and this technology was transferred into refractories applications.

Such fine aluminas could be added to LCCs to improve the particle packing density by deliberately filling further voids in the matrix's PSD (Particle Size Distribution), and furthermore partially, or even completely replacing commonly used silica fume. The precise manufacturing process of these specialty aluminas enables well controlled PSDs, so that the particle size distribution of matrix fine fillers can be steered accurately. This allows the design of tailor-made PSDs in the matrix down to the submicron range. The available product range of such reactive aluminas allows the combination of several monomodal grades to optimise the combination of different grain sizes

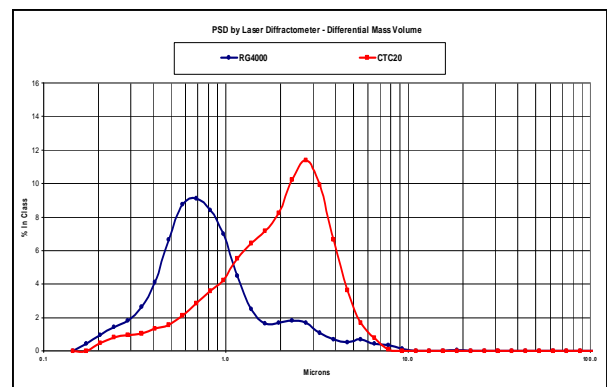


Fig. 6 PSD of mono-modal reactive aluminas RG 4000 and CTC 20

Significant improvements in the optimisation of particle packing can be achieved by the use of bi-modal reactive aluminas. The intensive batch milling process for these grades provides an ideal pre-distribution of the fine alumina crystal grain sizes, which results in lower water demand, faster wet-out times and improved overall castable properties. This demonstrates the advantage of bi-modal aluminas over a so called single component approach.

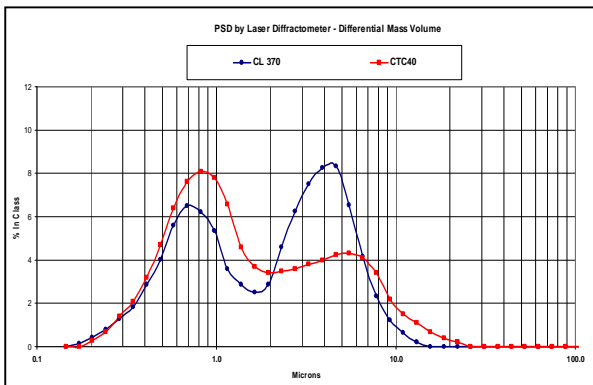


Fig. 7 PSD of bi-modal reactive aluminas CL 370 and CTC 40

One more important step was the development of multi-modal reactive aluminas. This was particularly driven by the requirements of self-flowing castables, which are even more demanding when considering matrix design.

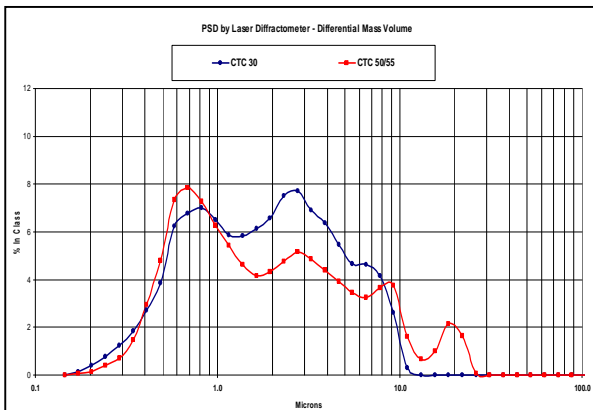


Fig. 8 PSD of multi-modal reactive aluminas CTC 30 and CTC 50/55

As self-flowing castables require a higher amount of matrix fines compared to vibration castables, fine milled ($-20\mu\text{m}$) tabular alumina with a low average particle size of about $3.5\mu\text{m}$ and an broad overall PSD can be used in combination with bi-modal or multi-modal reactive aluminas to further optimise the matrix fines particle packing.

5. High performance additive systems for low cement castables

In 1996, Almatix introduced the MAS (Matrix Advantage System) [10]. This brought on to the market a range of bi-modal and multi-modal reactive aluminas, and for first time showed the advantages of using a totally new additive product line, Dispersing Aluminas. The system allowed the development of silica fume-free, low cement tabular alumina and tabular alumina-spinel castables, requiring very low

mixing water demands of 4% and below. The specific properties of the dispersing aluminas ADS/ADW series products allowed, apart from high dispersion efficiency, a controlled adjustment of castable's working and demoulding time. This meant that castables could meet the different requirements resulting from different climate, placement condition, application and equipment. One more advantage of the dispersing aluminas is the addition level of about 1% to the LCCs. This delivers optimum homogeneity during the dry mixing of castables which had previously been dispersed with additives of 0.1% or even less.

Figure 9 compares various castable concepts in terms of CCS (Cold Crushing Strength) and HMoR (Hot Modulus of Rupture). It shows traditional CC (10% mixing water), commonly dispersed LCC (4.5% mixing water) and a LCC with fully optimised matrix alumina products and dispersing alumina (3.5% mixing water).

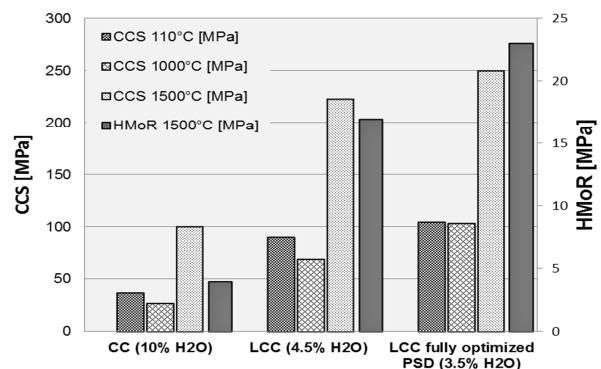


Fig. 9 CCS and HMoR of various castable concepts [11]

The fully optimised LCC system shows a tremendous improvement in mechanical strength and, in particular, hot properties. The usually seen strength drop at 1000°C , resulting from dissipation of the CAC's hydraulic bond, is therefore reduced in the optimised LCC concept.

6. Development of E-SY aluminas for robust and easy to use high-performance castables

As reactive aluminas and dispersing aluminas became key products in the matrix, ongoing development took place with particular attention given to the ease of mixing, quick castable wet-out and straightforward on-site installation with easy workability at lowest castable dilatancy. The reactive aluminas E-SY 1000 and reactive alumina-spinel E-SY 2000 were developed to fulfill the criteria for robustness-in-use castables [12]. The E-SY aluminas enable the development of vibration castables which exhibit

soft flow properties with aggregate sizes of up to 25mm. Their non-dilatant rheology enables the use of “light” mixing devices, e.g. common gravity mixers or similar low power equipment. These soft flow properties allow the castable to be transported or pumped over longer distances without the need for high pressure pumping equipment. **Fig.10** shows the discharge of a vibration LCC with tabular alumina T-60/64 6-15mm top size.



Fig. 10 Discharge of a vibration castable into a collecting container

7. Global product concept for Almatiss’ matrix aluminas

Almatiss, with manufacturing locations for its specialty alumina products in Europe, North America and Asia successfully introduced a global product concept for tabular alumina in 2005 [13].

The advantage of this idea is to offer the refractory manufacturer raw materials which are available globally with identical product properties and specifications. This accelerates the transfer of refractory technology and formulations between regions and eliminates the cost of re-formulation and re-qualification when qualifying different locally sourced products.

In addition, customers who are not structured globally can take advantage of this global product concept, because it provides security of supply by offering multiple sourcing.

In 2007 the Almatiss global product concept was extended to globally available matrix aluminas by introducing a harmonised PSD measuring method [14]. This covered the following alumina products: CT 800 FG, T-60/64 -20micron, RG 4000, CTC 20, CL 370, CTC 40, E-SY 1000 and CTC 50. The typical product data are listed in **table 3**.

Table 3 Typical product data global Almatiss aluminas for refractories applications

Properties/ method	Unit	CT 800 FG	T60/T64 - 20 micron	RG 4000	CTC 20	CL 370	CTC 40	E-SY 1000	CTC 50
Specific surface Area/BET	[m ² /g]	0.9	-	7.2	2.0	3.0	4.8	2.0	4.1
Particle Size/D50 Cilas	[µm]	3.5	2.0	0.6	1.8	2.5	1.2	1.7	1.5
Particle Size/D90 Cilas	[µm]	-	-	3.0	4.5	7.0	5.5	8.0	7.5
Grain size Distribution		-	-	mono-modal		bi-modal			multi-modal
Chemical Analysis									
Al ₂ O ₃	[%]	99.7	99.3	99.8	99.7	99.7	99.8	99.5	99.7
Na ₂ O	[%]	0.12	0.35	0.08	0.12	0.10	0.08	0.20	0.16
Fe ₂ O ₃	[%]	0.02	0.06	0.02	0.03	0.03	0.03	0.03	0.03
SiO ₂	[%]	0.02	0.10	0.03	0.03	0.03	0.03	0.03	0.03
CaO	[%]	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03

8. Conclusion

When reviewing castable developments over more than two decades, it is clear that fine matrix aluminas have become key elements for ongoing innovations in castable design. The development of these synthetically produced fine matrix aluminas, with their high chemical purity and consistent physical properties have enabled the development of low cement castables with a level of mechanical and hot properties which in the past could only be achieved by bricks.

The variety of ultra-fine and submicron fines-containing aluminas with mono-, bi- or multimodal particle size distributions offer the refractory engineer opportunities to develop tailor-made solutions in a wide field of applications in the refractory industry.

Ongoing developments in reactive aluminas, fulfilling the demand for robust and easy castable mixing and placement conditions at excellent mechanical and physical properties further support these innovative castable design efforts.

The global manufacturing and availability of Almatiss’ matrix aluminas contributes to ongoing trends in the global market place.

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