

GLOBAL PRODUCT CONCEPT FOR CALCINED AND REACTIVE ALUMINAS AND THE HARMONISATION OF PARTICLE SIZE MEASUREMENT

Andreas Buhr, Alexandra Friedrich, Rainer Kockekey-Lorenz*, Norbert Großmann, Rainer Egner
Almatis GmbH, Frankfurt/Main / Ludwigshafen, Germany

Tim A. Bullard, Robert W. Mc Connell
Almatis Inc., Bauxite, Arkansas, USA

William E. Smith
Almatis Inc., Leetsdale, Pennsylvania, USA

5

ABSTRACT

This paper reports about the implementation of a globally harmonised particle size measurement method and experiences gained during that process. It describes the decision steps used to select a globally introduced instrument and discusses the global Almatis calcined and reactive aluminas product range for applications in refractories.

INTRODUCTION

Calcined and reactive aluminas are required for refractory applications such as refractory bricks, sliding gates, vibration and self-flowing castables, gunning, shotcreting and ramming mixes. Almatis supplies a full range of calcined and reactive aluminas from Ludwigshafen, Germany, and two US manufacturing locations – Leetsdale, Pennsylvania and Bauxite, Arkansas (figure 1).

The Almatis global product concept has been developed to support the refractory customers in all regions worldwide to adapt to the ongoing trends in the global market place. These trends and their consequences have been discussed in detail by Buhr et al. [1] in 2005.

The global product concept for tabular alumina was introduced in 2001. Tabular alumina T60/T64 is available globally to the same specifications from 5 plants – Rotterdam, The Netherlands; Ludwigshafen, Germany; Leetsdale, US; Falta, India; and Qingdao, China. In the meantime, the global tabular product concept has proved its value in the global market place. The region-to-region technology transfer processes of our customers have become much easier; formulations do not need to be adjusted with regard to particle size distribution, if global tabular sizes are used. In addition, resources and time consuming additional testing and qualification of finished products by the end-user can be reduced or even avoided.



Fig. 1: Almatis manufacturing locations worldwide (Refractories, Ceramics and Polishing products)

Reactive aluminas in particular are key tools for modern refractory formulations, both castables and bricks.

They have a major impact on the water demand and rheological properties of castables and on the strength

porosity, and on the slag and wear resistance of the refractories. A change of these components in a refractory mix often requires an undesired, intensive re-qualification effort. The particle size distribution (PSD) of calcined and reactive aluminas is a key product property for this product line. Contrary to tabular alumina, which predominantly requires common screening for PSD characterization which seldom shows significant bias regardless of location and laboratory, the PSD measurement for calcined and reactive alumina is of much higher complexity. Different instrument types, either based on sedimentation principle or laser diffraction, show a significant bias for an identical product sample, the same can be observed between different laser diffraction instruments depending on supplier. For calcined and reactive alumina PSD characterization, Almatris used Micromeritics' Sedigraph, being historically more established, in North America and laser diffractometer from Cilas in Europe. Due to different PSD measurement techniques used, identical global PSD specifications could not be provided. Table 1 shows two reactive alumina grades as an excerpt from the previous global data sheet confirming the historical need for different PSD specifications for identical product.

Tab. 1: Excerpt from Global Product Data Calcines and Reactives

Properties/method	Unit	RG 4000			CL 370		
		typical	Min	Max	typical	Min	Max
Specific Surface Area/BET	[m ² /g]	7.2	6.0	9.5	3.0	2.6	3.4
Particle Size/D50 Cilas*	[µm]	0.8	0.5	1.0	2.6	2.0	3.0
Particle Size/D90 Cilas*	[µm]	4.0	2.5	6.0	9.0	5.0	13.0
Particle Size/D50 Sedigraph*	[µm]	0.5	0.3	0.6	2.9	2.2	3.4
Particle Size/D90 Sedigraph*	[µm]	2.6	1.0	3.5	6.4	5.0	8.0
Grain Size Distribution		mono-modal			bi-modal		
Chemical Analysis							
Al ₂ O ₃	[%]	99.8			99.7		
Na ₂ O	[%]	0.08		0.10	0.10		0.14
Fe ₂ O ₃	[%]	0.02		0.04	0.03		0.04
SiO ₂	[%]	0.03		0.08	0.03		0.07
CaO	[%]	0.02			0.02		

In order to offer key products within the calcined and reactive aluminas product line as global products to the refractory market, Almatris started a project in 2005 to harmonise their product properties and specifications in all regions locations with the target to select an identical instrument type at same settings for all manufacturing locations in North American and Europe.

ALMATIS' APPROACH TO THE GLOBAL PSD METHOD HARMONISATION

It is obvious that several global manufacturers of fine products in different markets have implemented global PSD measurement methods, however, at least due to non-availability of literature, Almatris is probably the first

company sharing in public the approach and experiences made for a global harmonised PSD measurement method. The first step in the project was the approval by the management for the related cost involved, including investment in the equipment required at a total cost of approximately US\$ 500.000.

Next a global team was formed comprising personnel from technical management, quality assurance and purchasing. The team established the important selection criteria as a "functional requirement specification" which the instruments should deliver as follows:

- Accuracy and reproducibility of results
- Assured day-to-day, region-to-region repeatability
- Broad PSD range covered, e.g. 0.04-300 µm
- Ability to properly detect mono-modal, bi- and multimodal PSD's
- Complete de-agglomeration achieved for measurement
- Short total runtime per measurement
- Robustness of equipment and user friendliness
- Global presence and service by instrument supplier
- Required accessories
- Guaranteed life cycle of instrument prior next model introduction
- Long term availability of spare parts
- Service by supplier and response time for repair and maintenance
- Availability of equipment for extended tests in our laboratories
- Number of units sold since instrument introduction
- Purchase price and service contract

The order of listing does not distinguish between aspects of lower or higher importance.

As different manufacturer's instruments provide different PSD results for identical samples, reproducibility and repeatability are considered as critical parameters regarding in-process control during calcined and reactive alumina production as well the final finished good control. This is very important as differences in results must be identified as being sample specific and not as instrument specific.

The old equipment-to-new-equipment bias also required revision of most existing specifications even though the product's particle size distribution did not change.

Approach to relevant PSD instrument suppliers

Following the definition of specific requirements, 7 potential instrument suppliers were contacted to make offers. Subsequently 5 suppliers were selected for further evaluation, sampled with a selection of aluminas for testing and invited to present their company, proposed instrument, specific features and sample

results in order to provide a first overview to the global team for further decisions.

Further project steps and experiences gained during the process

After careful and comprehensive evaluation of the 5 suppliers' presentations, instruments and handling features, initial sample results and the offers, the team narrowed down to 3 potential suppliers for further practical evaluation tests. This testing was done with 8 different alumina grades covering the desired PSD range from submicron fines into the upper range of about 250µm.

Reasons for not further considering the other suppliers or instrument types were for example general non-plausibility of initial sample results, e. g. what the result should be based on other product properties including specific surface area (BET) or top size by screening, general problems with insufficient sample de-agglomeration, cumbersome external sample preparation at very low sample weight per measurement and limited market penetration.

In the course of the project, the team decided not to consider PSD measurement by sedimentation principle. Considering the PSD range of the alumina products, several drawbacks were identified. For example the available sedimentation method based instruments being "blind" for coarser particles, not able to measure product mixes of components having different density e. g. alumina-spinel products, required cut-off in the submicron range to achieve reasonable measurement times and generally long runtime per measurement impacting cost and efficient laboratory resource utilisation.

Therefore it was decided to further evaluate the laser diffraction method only. This follows an observed general industry trend towards using laser equipment for fine particle size measurement.

Laser instruments require a selected algorithm to transform the laser diffraction into particle size distribution reading. When using this laser diffraction method, the ISO 13320 norm [2] recommends applying MIE theory for PSD measurement for particles below 50µm versus Fraunhofer theory. MIE theory however requires an imaginary factor which is material specific. No information was available from the instrument manufacturers or in literature on suitable factors and this method was not further followed. Note: Due to the product range to be measured including spinel, bonite, etc.; differing factors can be required for each and can lead to complex and cumbersome SOP's (Standard Operating Procedures). Additionally from experience there was no significant benefit from applying MIE theory including reactive alumina grades with high submicron particles proportion.

During the evaluation of practical results at the application laboratories of 3 potential suppliers, a strong focus was placed on proper sample dispersion in water prior measurement as very fine alumina products (<~1.5 microns) are agglomerated due to Van der Waals forces. Complete de-agglomeration requires, in addition to a dispersing agent, strong sonication. With partial de-agglomeration any instrument would identify the agglomerates as particles which would deliver a wrong reading on the particle size distribution.

Figure 2 shows the reactive alumina RG 4000 having more than 60% particles <1µm, that has been dispersed by stirring in water with dispersing agent. It reveals numerous large agglomerates far above primary crystal size and true particle size distribution.

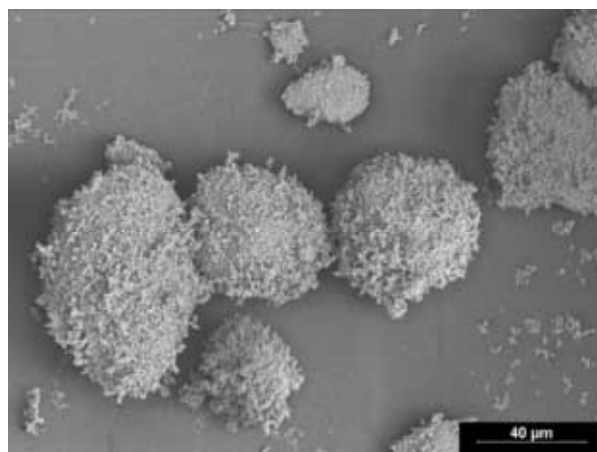


Fig. 2: RG 4000 insufficient dispersed by stirring in water

Only strong sonication at sufficient wattage leads to complete dispersion prior measurement and allows the instrument to detect the correct particle size distribution. Figure 3 shows the RG 4000 alumina completely dispersed.

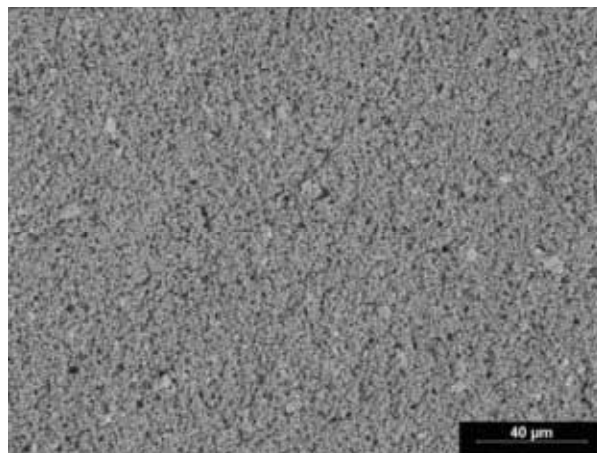


Fig. 3: RG 4000 completely dispersed by sufficient sonication

The design of the instrument should include a strong internal ultrasonic device that is part of or as a separate probe in the sample preparation chamber to avoid cumbersome and time consuming external sonication prior to sample addition to the instrument.

Figure 4 compares cumulative particle size distribution graphs of RG 4000 reactive alumina at sample preparation only by stirring in water without ultrasonic, ultrasonic at too low wattage and the correct fine mono-modal PSD only achievable at sufficiently high ultrasonic wattage. Sonication time is 120 s and applied at sample introduction and during the measurement.

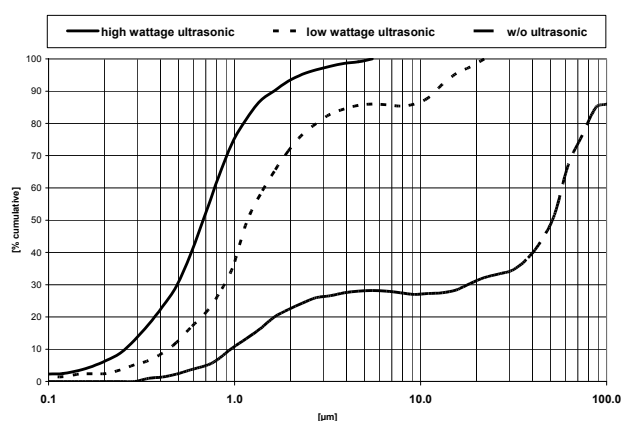


Fig. 4: RG 4000 cumulative PSD curves with and without sonication

Decision process, instrument selection and implementation

Following the reviews of sample results and the instrument specific preparation methods used for the 8 different samples provided to 3 potential suppliers' laboratories, the team did a careful and comprehensive evaluation of all parameters and instrument specific implications. Subsequently 2 potential suppliers were requested to provide instruments for a period of 6 weeks to the Almatris quality assurance laboratories in Germany and USA to allow extended in-house measurements with selected samples of locally produced aluminas as well as split identical samples to compare results from both laboratories, addressing the needs regarding region-to-region reproducibility and repeatability of results. During that period laboratory analysts had the opportunity to judge on how to operate the instrument including for example its user friendliness.

After evaluation of all aspects on how the instruments features fulfill the established "functional requirement specification" and comprehensive result comparisons supported by statistics, the global team decided to implement Cilas' 1064 laser diffractometer as the instrument for global particle size measurement

for all calcined and reactive alumina manufacturing locations concerned in Germany and USA.

The decision for instrument type was followed by purchasing the required units and their installation in the respective quality department laboratories.

A parallel measurement of old and new equipment was conducted for a period of 2 months which is required to cover all local and global products as well as in-process controls concerned. Comprehensive statistic evaluations of results were required and exploited to determine the product specification revisions required by the introduction of the new instruments.

The specification changes and implementation date were communicated in a notification letter to all customers for Almatris calcined and reactive aluminas.

GLOBAL CALCINED AND REACTIVE ALUMINA PRODUCT RANGE IN REFRACTORIES

The Almatris global calcined and reactive alumina product range currently includes the following products:

CT 800 FG: Medium crystalline ground alumina for manifold applications in shaped and unshaped refractory formulations including bricks and castables.

T60/64 -20MY: Product originally derived from the tabular alumina production route, however further processed like reactive alumina. It supplements to matrix fines reactive aluminas in high performing vibration and self flow castables and enables to achieve soft flow behaviour due to its broad particle size distribution.

RG 4000: Mono-modal reactive alumina with high amount of submicron particles for enhanced thermal reactivity and improved mechanical strength in high performance castables, pre-cast monolithic shapes and special dry pressed products.

CTC 20: Mono-modal semi reactive alumina specifically designed for silica fume containing castables.

CTC 50: Multi-modal reactive alumina for excellent flow properties in high performance, low water demand self flow castables.

CL 370: Versatile bi-modal reactive alumina for manifold applications in vibration and self flow castables, furthermore in special shaped products.

It is expected that the product range for global calcined and reactive aluminas will be expanded over time.

CONCLUSION

Following the key trend of globalisation in refractories manufacturing, Almatris has extended its range of global products by introducing global calcined and reactive aluminas. Further the drawback of

manufacturing location specific particle size distribution specifications has been eliminated by the implementation of a harmonised measurement method.

It is of high advantage to the refractory manufacturer to offer global raw materials with identical product properties and specifications as this accelerates the transfer of refractory formulations and eliminates cost for re-formulation and qualification as compared to local products use.

Also customers who are not globally structured take advantage of this global product concept, because it provides secure supply by multiple sourcing.

Growing the Almatix product range of globally available calcined and reactive alumina products contributes to standardisation which is and will be an important tool in the changing market.

REFERENCES

- [1] Buhr, A.; Graf, W.; Power, L.; Amthauer, K.: Almatix Global Product Concept for the Refractory Industry. Proceedings UNITECR 2005, Orlando/USA
- [2] ISO 13320-1 Norm