NABALOX® Bimodal Reactive Alumina

Influence of Reactive Alumina and Calcined Alumina on properties of free flowing castables

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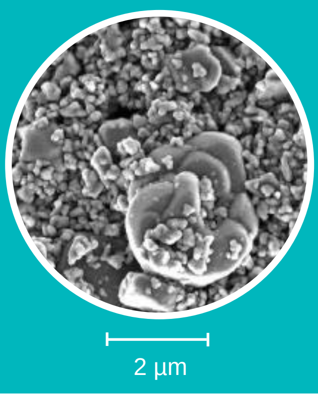

NABALOX®
Bimodal Reactive Alumina

Reactive Alumina is a well established group of raw materials for refractory castables to improve their rheological behavior. In this article the influence of bimodal Reactive Alumina and Standard (<325#) calcined Alumina on workability, packing density and strength of alumina based castables is examined. It will be shown that there is a significant effect on water demand and apparent density of the castable, which is depending on the percentage of Reactive Alumina on the one hand and on the type of Reactive Alumina on the other hand. The effect of the Aluminas on setting time and cold crushing strength has shown to be insignificant in this set of experiments.

- **Product properties**
  - High temperature resistance
  - Optimized processability
  - Bimodal
  - Homogeneous
- **Castable properties**
  - Very good flowability
  - Low water demand
  - High packing density
  - Low porosity
  - High corrosion resistance

1. Introduction

Castables are one major group in the field of unshaped refractories. They are often provided as a dry powder mix, water is added prior to placing. The consistency of the castable should allow pouring the refractory into shape without bubbles and other defects. Hydration of cement (usually Calcium-Aluminate-Cement, CAC) provides a temporary bond in order to remove the mold before heating up. To improve the hot properties of the refractories, there are two trends going on since several decades:

- Reduction of water content
- Reduction of cement
  (leading to low cement castables and ultra low cement castables)

The reduction of water leads to a higher packing density and thus lower porosity of the refractory [1]. However, it is limited to the need for a certain consistency. The reduction of cement can lead to higher refractoriness due to CaO-reduction. Cement reduction is limited because of the need for a proper early strength. What's more, a relation between porosity and strength links cement reduction to water reduction. Reduced porosity will lead to higher strength and thus, a lower demand for cement addition [2]. The key to achieve a good workable consistency is particle size optimization. Andreassen's packing model is a proper tool to visualize a castable's cumulative particle size distribution, enabling the engineer to adjust the recipe purposefully [3]. Especially modern bimodal Reactive Aluminas (RA) with primary crystal sizes of 2 µm and 0.5 µm have the ability to fill the smallest gaps between the cement particles (~ 10 µm) and common matrix fines like calcined -325# - aluminas. Consequently, the use of bimodal Reactive Alumina leads to increase of particle packing density by obtaining good flowing properties already at very low water contents of the castable. [4,5] This effect results in higher strength, lower high temperature shrinkage and better resistance to corrosion and infiltration of corrosive media like steel making slag. The application of superplasticizers plays a crucial role in the extensive use of ultrafine Aluminas [6].

The experiments described in this paper have been designed to illustrate the effect of two systematic variations of a castable's formulation.

A: To screen the amount of bimodal Reactive Alumina from 2 % to 13 %.

B: To make a comparison between a well-established bimodal Reactive Alumina and a newly developed bimodal Reactive Alumina, that is designated to achieve lowest viscosity in free flowing castables.

2. Experimental procedure

2.1. Raw material choice

The test castables where formulated with sintered alumina aggregates (Tabular Alumina, TA, Alfa Tab, Silkem Slovenia), Calcium aluminate cement (CAC, Secar 71, Imerys Aluminates, France) and Calcined and Reactive Alumina (CA and RA, **NABALOX®** Nabaltec AG, Germany). As a super plastisizer a Polyacrylate (PAE, Viscocrete 225 P, Sika, Germany) was used.

2.2. Castable formulation

For the first variation, four castable formulations where created (see table 1), by subsequently reducing the amount of RA from 13 % to 2 % and at any one step increasing the amount of CA and TA. What's more, from formulation 2 to 3, the TA size 0 – 0.3 mm was eliminated and CAC was increased from 3 % to 5 %. This was done in order to compensate the strength breakdown resulting from RA-reduction.

For the second variation, two combinations of a 325#-grade alumina with one bimodal Reactive grade Alumina were predefined: Matrix A, promising lowest water demand, and Matrix B in expectance of slightly higher water demand, but still reasonable properties.

Table 1: Castable formulations according to the first variation

Formulation		1	2	3	4
TA 3 – 6 mm	[%]	24	24	24	24
TA 1 – 3 mm	[%]	16	16	16	16
TA 0.5 – 1 mm	[%]	15	15	15	15
TA – 0.5 mm	[%]	7	8	11	11
TA – 0.3 mm	[%]	5	6		
TA – 325#	[%]	12	14	15	15
CAC	[%]	3	3	5	5
CA	[%]	5	7	8	12
RA	[%]	13	7	6	2
PAE	[g/100g]	0.1	0.1	0.1	0.1

Table 2: Physical and chemical properties of the used CA and RA grades, according to the second variation

		Matrix A		Matrix B	
		CA (-325#)	RA	CA (-325#)	RA
		NO 315	NO 530	NO 115 TC	NO 660
D_{10}	[µm]	0.8	0.3	1.0	0.4
D_{50}	[µm]	3.2	1.6	4.5	1.9
D_{90}	[µm]	8.5	5.0	13	5.0
$S_{spec.}$	[m²/g]	1.2	4.0	0.9	2.8
Al_2O_3	[%]	99.6	99.8	99.6	99.8
Na_2O	[%]	0.30	0.10	0.30	0.10
SiO_2	[%]	0.02	0.02	0.01	0.02

While matrix A was only tested in formulation 1 to 3, matrix B was tested in all four formulations.

2.3. Raw material characterization

All Calcined and Reactive Alumina grades were characterized with regard to grain size distribution (laser diffraction, Cilas 1064, Micromeretics), specific surface (S_{spec}, BET, DIN ISO 9277), chemical composition (ICP/OES, SpectroBlue, SPECTRO Analytical Instruments GmbH).

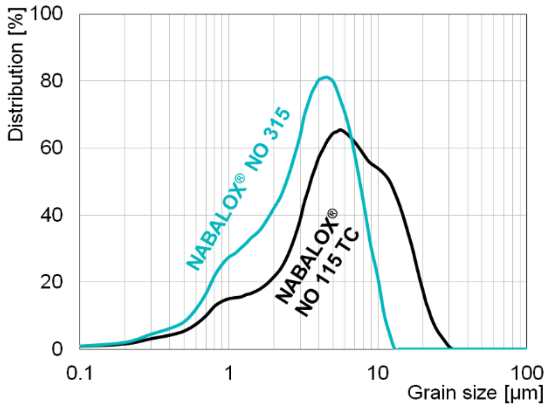

Figure 1: Particle size distributions of the CA-grades

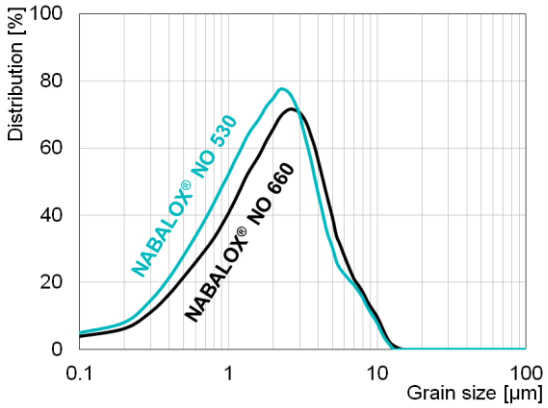

Figure 2: Particle size distributions of the RA-grades

The powder parameters are highlighted in table 2, figures 1 and 2 illustrate the particle size distributions. For matrix A, both, the 325#-grade CA and the RA is finer and more reactive, in comparison to matrix B. For CA the difference can be described as follows: The D_{90} of **NABALOX®** NO 315 is significantly lower, compared to NO 115 TC, which indicates a better disaggregation of NO 315. This property promises lower water demand due to a lower amount of remaining aggregates. For the RA grades, there is no difference in D_{90}, indicating that both powders are assumed to be free of remaining aggregates. For the RA grades, the difference is rather obvious in D_{50} and $S_{spec.}$ For NO 530, D_{50} is lower and S_{spec} is higher than for NO 660, indicating a higher amount of submicron-particles that are able to fill the smallest gaps between the matrix particles and thus replacing water. Those differences promise lower water demand and lower viscosity for the formulations containing matrix A.

2.4. Castable tests

Spreading of the castables was measured under free flowing conditions according to ISO 1927-4:2012 and strength evolution during the first 24 h was monitored by measuring the ultra sound velocity (IP8-measurement system, Ultratest GmbH). The time to exceed a sound velocity of 1500 m/s was defined as the setting time. The castable was vibrated into cylindrical molds having a diameter of 36 mm and a height of 36 mm. Samples have been hydrated in a climate chamber at 20°C and 90 % relative atmospheric humidity for 24 h before unmolding. Cold compressive strength of the cylinders was measured according to DIN EN 196-1:2005-05 after drying for additional 24h at 110°C ($CCS_{110°C}$). Apparent density was calculated from the mass and the volume of the cylindrical samples after drying.

3. Results and discussion

3.1. Water content

Tables 3 and 4 give an overview on the results. The first and most important result is the effect on water demand. The water content of each castable had to be evaluated separately in order to achieve the same consistency, which was defined as a spreading between 100 % and 130 %. (Only formulation 2 with matrix A is listed with poorer consistency. The spreading value was above 130 % with 4.0 % of water and below 100% with 3.8 %. The test has not been repeated with 3.9 %.)

Table 3: Castable properties achieved with matrix A

Formulation		1	2	3
Water demand	[ml/100g]	3.8	3.8	4.0
Spreading	[%]	125	95	120
Setting time	[min]	600	210	170
CCS $_{110°C}$	[MPa]	73	90	97
Apparent density$_{110°C}$	[g/cm³]	3.31	3.34	3.26

Table 4: Castable properties achieved with matrix B

Formulation		1	2	3	4
Water demand	[ml/100g]	4.0	4.2	4.4	5.2
Spreading	[%]	110	120	110	110
Setting time	[min]	220	210	180	340
CCS $_{110°C}$	[MPa]	61	59	74	70
Apparent density$_{110°C}$	[g/cm³]	3.29	3.25	3.20	3.18

3.2. Influence of Reactive Alumina percentage (first variation)

The Reactive Alumina content is an essential tool to adjust a castable's water demand in a wide range. As shown in figure 3, the dependence is not linear. In order to simplify the course of the curve, the assumption was made that the dependency is linear for RA contents from 2 % to 7 % with a high negative slope and also linear from 7 % to 13 % with a lower negative slope.

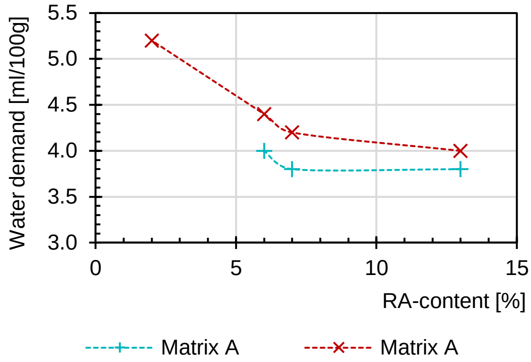

Figure 3: Water demand of the test-castables in dependence of the Reactive Alumina content

The slopes, calculated by rough linear interpolation are -0.2 for RA-contents below 7 % and -0.03 for RA-contents from 7 % to 13 %. The unit of the slope is $\frac{ml/100g\ (Water)}{\%\ (RA-content)}$.

What's more, a clear dependency between water content and apparent density can be observed independently from the matrix. Figure 4 shows a rather small increase in apparent density for a significant water reduction from 5.2 % to 4.4 % on the one hand and an impressive density increase for further water reduction down to 3.8 % following a linear curve on the other hand.

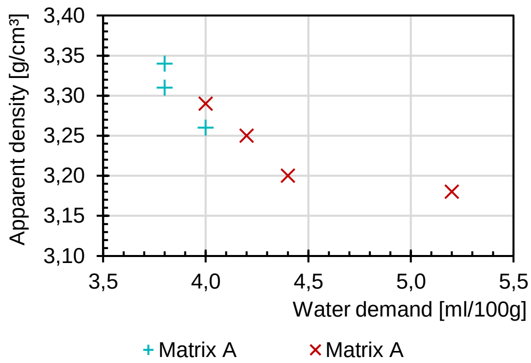

Figure 4: Apparent density of the test castables in dependency of the water demand

From these results, the following conclusion can be made: Increasing the Reactive Alumina percentage in a castable's formulation results in a continuous improvement of properties. Even though increasing the Reactive Alumina content from 7 % to 13 % will allow only 0.1 % - 0.2 % water reduction, a noteworthy increase in density will be the result, followed by numerous positive effects like increase of hot and cold mechanical properties, infiltration resistance, wear resistance, just to name a few.

3.3. Influence of Calcined and Reactive Alumina grade (second variation)

As can be read from table 2, both aluminas, CA and RA, respectively, have lower particle sizes for matrix A in comparison to matrix B, and thus, matrix A promises lower water demand. This expectation is fulfilled for all formulations, as can be seen in figure 5. Furthermore, the density increase, as an indirect consequence of the Reactive Alumina exchange is obvious, illustrated in figure 6.

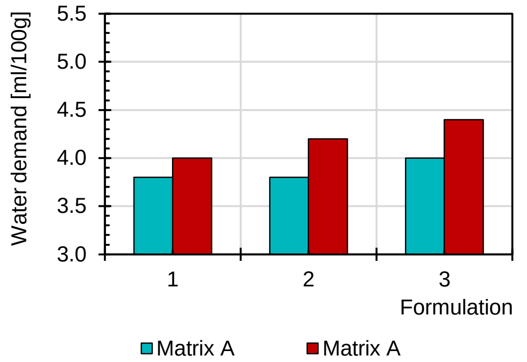

Figure 5: Influence of the matrix on water demand of the test castables

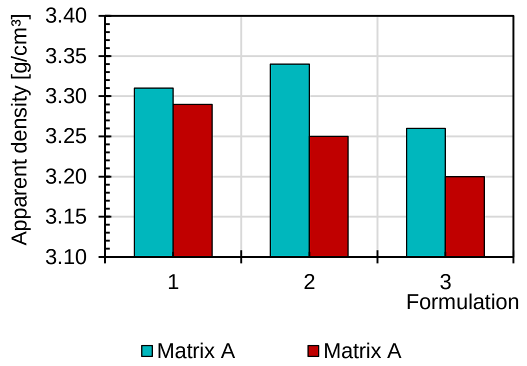

Figure 6: Influence of the matrix on apparent density of the test castables

It is assumed, that there is an optimum amount of submicron particles in order to provide best flow and highest packing density at lowest water demand. Figure 6 leads to the conclusion, that this optimum is already exceeded, if 13 % of **NABALOX®** NO 530 is used, while 13 % of NO 660 does still not provide lowest water demand.

From another point of view, as long as lowest water demand is not required, Alumina matrix A can provide the same properties as matrix B, but with a lower content of Reactive Alumina. This offers a tool to develop more cost efficient formulations with a reduced content of Reactive Alumina.

3.4. Cold crushing strength and setting time

No significant correlation between RA-content and CCS can be observed. The same applies for setting time. In this context, formulation 1 with alumina matrix A should be classified as an outlier with an unexpected long setting time and low CCS. What's more, there is a jump in water demand from formulation 2 to formulation 3, not due to RA-content, but due to the total change of the castable's PSD. This jump theoretically would be accompanied by a strength decay, which is compensated by the increase in CAC-content, that's why no strength decay was observed here.

4. Summary

Reactive Alumina is a proper way to reduce water demand of castables and, as an indirect consequence, to increase the apparent density of the same. It could be shown, that although the water reducing effect is decreasing with higher percentages of Reactive Alumina, the apparent density continues to rise in a linear way. Besides the amount of Reactive alumina it could also be shown, that the grade of reactive alumina has a similar effect. Instead of increasing the amount of Reactive Alumina, switching to a different, more reactive grade has the same effect on water demand and apparent density.

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