## THE ROLES OF MATRIX ALUMINAS ON THE PROPERTIES OF HIGH PERFORMING REFRACTORY CASTABLES

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#### ABSTRACT

Decades back only ground calcined alumina was the choice of high-alumina matrix products that were used in castable formulations. At that time the flow properties of castables were enhanced by the use of silica fume. However, silica fume, later was avoided in high performing castables because of inferior high temperature thermo-mechanical properties above 1400°C. Then the development of new generation castables came by using fully ground reactive aluminas for high temperature applications such as steel ladle well blocks, seating blocks, RH snorkel or porous plugs etc. It is well established before many a times that high alumina castables (such as medium/ low/ ultralow cement castables) containing higher Na<sub>2</sub>O, especially in matrix ingredients, show inferior high temperature properties in Al<sub>2</sub>O<sub>3</sub> - Na<sub>2</sub>O - CaO system. However, the choice of those reactive aluminas or matrix aluminas in new generation high performing castables are certainly not limited to chemical purity but mainly to the physical properties such as specific surface area (BET) and particle size distribution (PSD). A wide range of reactive aluminas of different PSD and varied specific surface areas were selected to observe their effects on the rheology, workability, volume and structural stability, cold and hot strengths of high alumina low cement castable. The optimum choice of such matrix formulation provides proper rheology and setting requirements as well as excellent mechanical and physical properties to support the demands of high temperature applications.

In this present work four different kind of matrix aluminas were selected on the basis of  $d_{50}$  and surface area. Rheological study and setting properties along with all other properties like AP, BD, CCS, volume stability etc. were studied. Different mineralogical phases were identified by XRD and microstructure analysis was carried out by optical microscope for some specific samples to understand the properties after firing at different temperatures.

# Key words: castable; matrix; reactive alumina; rheology; strength

#### INTRODUCTION

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. However, the initial formulations with silica fume as superfine matrix component resulted poor refractoriness and thermo-mechanical stability and therefore this limits the use in high performance applications [1]. This was followed later by the development of fully ground reactive aluminas which contributed to the design of the matrix below 63µm. The needs for fully ground bi-modal and multi-modal reactive aluminas have grown with the development of low cement, ultralow, and no cement castables. Such fine aluminas could be added to LCCs to improve the particle packing density by deliberately filling further voids in the matrix. These matrix aluminas are used in achieving the specialized particle size distributions that are required to achieve the desired physical properties and placement rheology. Many papers and articles have been published [2, 3, 4] documenting the need for controlled particle size distribution (PSD) in both the refractory aggregate materials (down to  $\sim$ 75µm/ 200mesh) and the fine refractory matrix materials.

The performance of castables to a large extent is dependent on the characteristics of the raw materials used in the castable formulations. High purity raw materials such as Tabular Alumina and Magnesium Aluminate Spinel are widely used in the high performance demanding applications such as RH snorkel, porous plug, seating block, well block and steel ladle linings etc. Many a times, due to the type of production design and castable usage, these castables for demanding applications are of self-flow type which is driven by specific rheology. And the castable rheology is mainly defined by the matrix composition particularly below 45 µm, which directly related to co-efficient of distribution factor as per Andreasen equation. In case of self-flowing castables higher amount of fines is required than vibration castables [5, 6]. The matrix part of a refractory castable is usually composed of four kinds of raw materials such as calcined or reactive alumina (or silica fume, not considered because of high performance demand), calcium aluminate cement, additives (e.g. dispersing aluminas), Tabular Alumina or other fines. Although a LCC self-flow type castable formulation contains  $35\pm5\%$  of matrix components [7], their behavior strongly determines the castables performance in respect of:

- a) Rheology (flowability, flow-decay, setting time)
- b) Strength (curing strength at room temperature, drying strength at 110°C and hot strength)
- c) Volume stability at high temperatures
- d) Resistances to abrasion and thermal spalling

A reactive alumina added in matrix is supposed to control and affect all the above properties in castable and determine the extent of self-flow behavior in application. Although low dilatancy castable is generally an advantage for easier vibration installation in application but it is difficult to achieve very low dilatancy of high purity self-flow low cement castables containing Tabular and Spinel. However, low dilatancy is an essential criteria for certain specific applications of self-flow castables (e.g. shotcreting or selfflowing installations). A reactive alumina is characterized by different parameters like low soda content (Na<sub>2</sub>O  $\approx <0.15\%$ ), high  $\alpha$ -alumina content ( $\approx$  >95%), specific surface area (BET) and specific particle size distribution (PSD). The reactive aluminas used in this work, differ in BET and PSD. It is expected that the differences in BET and PSD will generate different overall distribution in fines followed by sintering which is expected to affect castable properties and performances.

#### EXPERIMENTAL

Four batches were prepared with fixed dosage of four reactive aluminas (RA1, RA2, RA3 and RA4) having different PSD and BET. In order to make a comparison another batch was prepared with superfine tabular alumina ( $<20\mu$ m) as TA5 replacing reactive alumina having similar BET. RA3 and RA4 are specially engineered reactive aluminas. The chemical and physical properties for different reactive aluminas and tabular alumina superfine are shown in Tab.1 and batch formulations are given in Tab.2.

Tab.1: Typical properties of selected reactive alumina

	RA1	RA2	RA3	RA4	TA5
$D_{10}$ , $\mu m$	0.1	0.2	0.4	0.2	0.3
$D_{50,}\mu m$	0.6	1.3	1.5	2.4	2.2
D <sub>90,</sub> µm	2.6	5.3	6.8	6.9	13.6
< 1 µm, %	69.2	42.9	33.4	30.8	32.6
BET, m <sup>2</sup> /g	7.40	4.68	3.60	3.01	3.51
Al <sub>2</sub> O <sub>3</sub> , %	99.82	99.84	99.71	99.82	99.59
Na <sub>2</sub> O, %	0.07	0.09	0.06	0.11	0.27
SiO <sub>2</sub> ,%	0.02	0.02	0.04	0.02	0.05
Fe <sub>2</sub> O <sub>3</sub> , %	0.02	0.02	0.03	0.02	0.03

Tab.2: Different batch formulations

(figures in %)	RA1	RA2	RA3	RA4	TA5
WTA	50	50	50	50	50
Spinel +1mm	10	10	10	10	10
Spinel -1mm	26	26	26	26	26
RA1	8				
RA2		8			
RA3			8		
RA4				8	
TA5					8
HA Cement	5	5	5	5	5
Dispersants	1	1	1	1	1

Different batches of 10kgs were made in Hobart Mixer with 1 minute dry mixing followed by water addition and wet mixing for another 4 minutes. For a simple matrix of comparison, water addition was restricted to 5.5% for each formulation (although, in actual, water demand could vary significantly with different reactive aluminas). Flow decay (self flowability) for all samples were measured up to 90 minutes with an interval of 30 minutes with at controlled temperature of 20°C and controlled storage of 60% RH. CCS (cold crushing strength), CMOR (cold modulus of rupture), BD (bulk density), AP (apparent porosity) and PLC (permanent liner change) were measured from cast bar of size 160mm x 40mm x 40mm. Initially all samples were cured at room temperature for 24 hours and then dried at 110°C for 24 hours. Firing was carried out at 800°C, 1100°C, and 1600°C with 3 hours soaking. In case of PLC measurement initial length was taken after drying at 110°C for 24 hours. AP and BD both were measured as per Archimedes Principle by water displacement method. Repeat PLC and AP were measured up to five times at 1600°C with 3 hours soaking. Hot MOR was measured with the sample of size 150mm x 25mm x 25mm at three different temperatures (1300°C, 1400°C and 1500°C) with 30 minutes soaking time. Samples for HMOR were prepared after pre-firing at that particular temperature for 3 hours. XRD analysis of selected samples were carried out with the samples fired at 1500°C. Abrasion loss was measured as per ASTM C704 standard after prefiring the samples at 800°C for 3 hours. Thermal spalling resistance was measured with dried (110°C/ 24hrs) cube samples of 65mm x 65mm x 65mm size through in-house standard of water quenching method. Initially samples were put inside the furnace and raised the temperature to 1300°C. After holding the samples for 30 minutes, they were taken out from the furnace and immediately immersed into cold (20°C) flowing water and kept for 5 minutes inside the water. Then samples were taken out, put in a drier at 110°C for 10 minutes and again put inside the furnace where temperature is maintained at 1300°C. This cycle was repeated until there was cracking and breakage of the samples into pieces. Microstructures for selected fired (1500°C) samples were checked in optical microscope.

#### RESULTS AND DISCUSSION

Rheology and flow behavior is one of the foremost criteria in high purity self-flow castable. In most of the cases flowability is most important to get the homogeneous cast body without any internal defects. The behavior of flow decay is shown in Fig.1. The nature of flow decay is almost similar for all four kinds of reactive aluminas but RA3 showed a significantly higher flow and lower flow decay. On the other side, in case of WTA superfine ( $<20\mu m$ ), the initial flow value was less as well as sharp flow decay observed with ~50% flow still remains after 90 minutes. The flowability depends not only on d<sub>50</sub> and surface area but also on matrix particle size distribution. In case of reactive aluminas, the distribution of particles is different than <20µm tabular alumina which differentiates the flow decay in longer duration. The other part of castable rheology is mixing wetout time and setting behavior as showed in Tab.3. A lower wetout time is an indirect control over mixing uniformity. Thus proper reactive with higher surface area and finer particle size distribution could be advantageous. The exothermic setting behaviors indicate that reactive alumina with finer PSD and higher BET may have an earlier setting property although flowability could be in similar range. Here Exo-Max can be referred as end of cement hydration reaction which means typically the safety period prior to demoulding of the casted mix. RA1 could be advantageous among selected mix formulations. Type of mix dilatancy was higher with RA2 and RA4 where as RA1 and TA5 showed lower dilatancy. Castable mix with RA3 showed very low dilatancy which is very much favourable for casting the selected type of self-flow castable. This is due to the specially engineered PSD of RA3.



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	RA1	RA2	RA3	RA4	TA5
Wetout	30 s	45 s	45 s	60 s	90 s
time					
Exo	195	220	264	260	NA
start1	min	min	min	min	
Exo	6.1h	9.1h	7.5h	10.2h	10.9h
start2					
Exo	8.7h/	11.9h/	10.9h/	14.4h/	14.6h/
Max	20.8C	21.1C	21.6C	20.2C	20.8C
Dilatan	Low	High	Very	High	Low
су			low		

Bulk density. CMOR and CCS for all samples are shown in Fig. 2, 3 and 4. After drying at 110°C, BD is higher in all cases as only free water got removed till that period. With increasing firing temperature, there is decrease in BD up to 900°C due to remove of the chemically combined water present in the castable. The same trend continues till 1100°C when development of new ceramic bonds starts after

complete elimination of hydraulic bonds. Thus BD has again increased after firing the samples at 1600°C which is a result of sintering followed by shrinkage.







While measuring CMOR and CCS, the trend is also similar for all kinds of reactive aluminas. There is no significant change in CMOR and CCS up to the firing temperature of 1100°C. But there is significant increase in CMOR and CCS while firing the samples at 1600°C. This increase in strength was observed while firing the samples >1100°C and is due to ceramic sintering. At 1600°C, in case of sample having superfine tabular alumina <20µm (TA5), both CMOR and CCS are much lower than other samples with same amounts of reactive aluminas. This clearly indicates that reactive aluminas enhance the sintering at relatively lower temperature due to their specific particle size distribution and inertness of completely sintered aggregate Tabular alumina at that temperature compared to other aluminas calcined at much lower temperature during manufacturing. One interesting observation is that for RA4 sample both CMOR and CCS are maximum at 1600°C though the d50 is more and BET is less compared to other three reactive aluminas. This is due to the specific engineered PSD of RA4 reactive alumina which helped the matrix for stronger bonding with the aggregates.

PLC for all samples were measured after firing at 800°C, 1100°C and 1600°C with 3 hours soaking but there is negligible change in shrinkage. On the other hand, repeat PLC was measured at 1600°C with 3 hours soaking till 5 cycles to observe further scope of sintering. A continuous shrinkage was observed for all samples (Fig.5) except TA5 because of inertness of tabular alumina superfine (<20µm). RA1 gave highest and significant shrinkage in all the cycles probably due to almost 70% particles is below 1µm size and it's higher BET. RA2, RA3 and RA4 showed similar shrinkage trend and the degree of shrinkage is reducing after 3 cycles onwards. The overall trends signify that the degree of sinter reactivity is related to PSD patterns in the reactive aluminas used.



Fig.5. Repeat PLC at 1600°C for different samples

HMOR for different samples measured at three different temperatures are shown in Fig.6. It is observed that at 1300°C when only partial sintering of the materials took place and hot strengths are lower in all cases. The maximum HMOR is recorded at 1400°C for all samples including the sample having tabular alumina <20 $\mu$ m (TA5). This means sufficient sintering is taking place at 1400°C. However, at 1500°C, the temperature effect is predominant over the sintering effect and is common for all samples. In case of TA5, HMOR is lower because of absence of reactive alumina and higher Na<sub>2</sub>O in it.



Fig.6. HMOR measured at 1300°C, 1400°C and 1500°C



Fig.7. Thermal spalling from 1300°C to water

Thermal spalling results are shown in Fig.7. There was slight difference in thermal spalling resistance trend among different reactive aluminas. The samples with RA1 and RA2 exhibit slightly better thermal spalling resistance in terms of crack formation and propagation. The reason could be relatively higher BET in RA1 and RA2.



Fig.8. Abrasion loss for different samples

Abrasion resistance of the sample depends on the bonding of matrix with aggregate. It was expected that a strong matrix design will have good abrasion resistance behavior. The abrasion loss values are shown in Fig.8. The maximum abrasion loss was observed for sample RA3 and TA5. RA3 has a special engineered PSD which was advantageous for low dilatancy but not became so effective in abrasion resistance compared to others. For TA5, absence of any reactive alumina causes poor bonding with the aggregates and hence its abrasion resistance is also inferior. RA2 and RA4 showed similar abrasion resistance whereas RA1, having narrow PSD with minimum  $d_{50}$  and maximum BET, gave the best abrasion resistance.



Fig.9. XRD of RA1 and TA5 after firing at 1500°C



Fig. 10. Optical microscopy for RA1 (left), TA5 (right)

In XRD (Fig.9) the major phases are corundum and spinel. The XRD pattern for other samples is similar like RA1 and therefore not shown here. While doing the optical microscope for matrix of both for RA1 and TA5 after firing at 1500°C, some difference is observed. For RA1, reactive with high BET and highest amounts of particles with below  $1\mu m$  size, the spinel grains are uniformly distributed throughout the

matrix; Where as in case of TA5, the distribution is not so uniform (Fig.10). This is probably due to the comparative inertness of Tabular alumina than reactive alumina at 1500°C and comparatively lower amounts of particles with below 1 $\mu$ m size. The higher HMOR in case of RA1 and RA2 both at 1500°C and 1400°C are also related to the same reasons mentioned here. Thus the usage of superfine of TA (<20 $\mu$ m) should not be considered as alternative of reactive alumina. Rather, addition of TA (<20 $\mu$ m) could be considered as supplement to matrix alumina formulation although it's effect is not covered in this work.

#### CONCLUSIONS

Flow and flow decay of castables depend upon the nature of superfine materials in matrix to give optimum particle size distribution. In occasion, engineered reactive alumina fulfills the demand for placement conditions with excellent mechanical and physical properties which further support innovative castable design efforts. Physical and other thermomechanical properties particularly HMOR depend on PSD pattern and specific surface area of selected reactive alumina. Matrix compactness with aggregate is very essential to get good abrasion resistance. Thermal spalling resistance indicated that reactive alumina with higher surface area could be beneficial. The quantity of sub-micron particles presence in the mix determines castable shrinkage property. Though d<sub>50</sub> and specific surface area of tabular alumina superfine (<20µm) could be similar to a reactive alumina but there are significant differences in flowability, rheology and other physical and high temperature properties due to reactivity difference. Thus it could be used in addition to reactive alumina to get further value enhancement in castable properties although it was not considered here. The variety of ultra-fine and submicron fine containing reactive aluminas offer an opportunities to develop tailor-made solutions focusing specific property demands in the wide field of high performance castable applications. This whole study was subjected to fixed dosage of reactive alumina in a selected formulation with fixed water addition. Nevertheless, a higher dosage of reactive alumina with varied water demand is expected to act differently in flowability and other physical properties.

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