The Role of Granulometry and Additives in Optimising the Alumina Matrix in Low Cement Castables

J. Kiennemann, E. Chabas, C. Ulrich, D. Dumont

Fine particles play a major role not only in the flowing characteristics of castables but also in the final properties of the castable in application. To optimise the particle packing of the castable, different kinds of fine aluminas can be used to form the matrix: calcined, semi-reactive, monomodal reactive or multimodal reactive aluminas. A systematic approach has been conducted to investigate different ways to optimise particle size packing in low cement castable formulations thanks to the use of different kinds of aluminas. Typical average particle size for these aluminas ranges from 0,3 µm to 6 µm. The potential of a new alumina product has been explored as a competitive alternative to reactive alumina. It has a median particle diameter (d_{50}) around 3 µm and has a monomodal granulometry with some fines particles around 0,5 µm coming from its specific milling technology. Dinger and Funk's packing model has been used to optimise packing design of the castable with this alumina. In many cases the sole use of this alumina in the formulation can be fully satisfying for the application. In other cases, the combination with a reactive alumina (d_{50} = 0,5 µm) is useful to further improve rheological properties. Bimodal aluminas are usually found to be very efficient to achieve good rheological properties and high levels in applicative refractory tests. The effects of the particle size curve have been investigated to understand the impact on castable properties. Flowability behaviour and torque evolution during mixing have been followed to characterize rheology. It will be shown that differences between various aluminas can be compensated by usage of specific additives.

1 Introduction

Refractory formulations contain a combination of coarse aggregates, fine aggregates and matrix fines. Coarse particles form the skeleton of the castable and fine aggregates fill the large voids between the coarse aggregates. And the matrix fines fill the small micron size voids. To optimise the performance of refractories, the right combination of raw material has to be chosen. The particle packing in the castable highly impacts the refractory performance in terms of mechanical, chemical and thermal shock resistance. That is why particle size distribution in the castable is so important to optimise. Andreasen [1] has given a model, improved by Dinger and Funk [2–3], for continuous particle size distribution optimisation. Although a castable formulation only contains about 20–30 % of matrix components, their behaviour strongly determines the castable performance in terms of flowability, density, strength and corrosion resistance. Alumina fines play a major role in the flowing characteristics of castables [4] and this study investigates the way alumina specific particle size distribution (PSD) can modify these characteristics. A statistical study with various calcined alumina shows that the flowability is improved when decreasing the median grain size of the calcined alumina. What is also interesting is that at the same d_{50}, the flowability is improved by reducing the d_{90} of the calcined alumina. This result gives interest to fine calcined product with d_{50} about 3 µm and a reduced d_{90} that could be obtained thanks to a new continuous milling system. Achieving flow at low water demand has received a lot of attention in recent years through investigation in the field of additives for refractory castables, in order to develop a range of technologies such as pumping, self-flow, shotcreting. Yet, no single universal deflocculating system exists [5]. This is due to the different solubility and surface charges of the fine particles of the matrix that can affect the interaction with the dispersant. This point will be checked in the study by changing the kind of alumina in the castable with two different additives.

Jérôme Kiennemann, Elodie Chabas,
Carol Ulrich, David Dumont
ALTEO
Gardanne
France

Corresponding author: *J. Kiennemann*
E-mail:
jerome.kiennemann@alteo-alumina.com

Keywords: low cement castables,
bimodal aluminas, flowability

2 Alumina raw materials

Calcined alumina (C) and reactive alumina (B for bimodal reactive alumina and MR for monomodal reactive alumina) have been processed by Alteo for this study (Tab. 1).

Two industrial ground calcined aluminas C1 and C2 have been used in low cement castable (LCC). They have similar d_{50} but different particle size distribution shapes. Alumina C1 has a coarser distribution but also less fine particles than C2. C1 has a d_{90} and a d_{10} much higher than C2. To differentiate the respective effect, Alumina C3 and C4 have been processed. Alumina C3 was obtained through a sieving of C1 alumina in order to fit at best the coarse part of the particle size of alumina C2. Alumina C4 was obtained through a dust removing of alumina C2 in order to fit at best the fine part of the particle size distribution of alumina C1 (Fig. 1).

Bimodal reactive alumina B1 to B5 have been processed by cogrinding two aluminas with respective crystal size of 2 µm and 0,5 µm in a batch ball milling. By varying the grinding at a constant ratio of coarse and fine alumina, different particle size distribution curves have been performed (Fig. 2).

Tab. 1 Physical and chemical characteristics of used alumina

	Calcined Alumina				Bimodal Alumina					
	C1	C2	C3	C4	B1	B2	B3	B4	B5	MR
Na_2O [ppm]	2500	2300	2500	2300	400					550
SiO_2 [ppm]	145	175	145	175	600					500
Fe_2O_3 [ppm]	145	120	145	120	150					110
d_{10} [µm]	1,42	1,27	1,40	1,40	0,48	0,48	0,48	0,57	0,32	0,2
d_{50} [µm]	3,05	3,15	3,02	3,25	2,34	2,34	2,12	2,41	2,28	0,5
d_{90} [µm]	10,8	6,8	8,2	6,7	5,24	12,4	4,94	5,55	5,11	1,8
BET [m²/g]	1,45	1,40	1,45	1,40	2,7					6,7

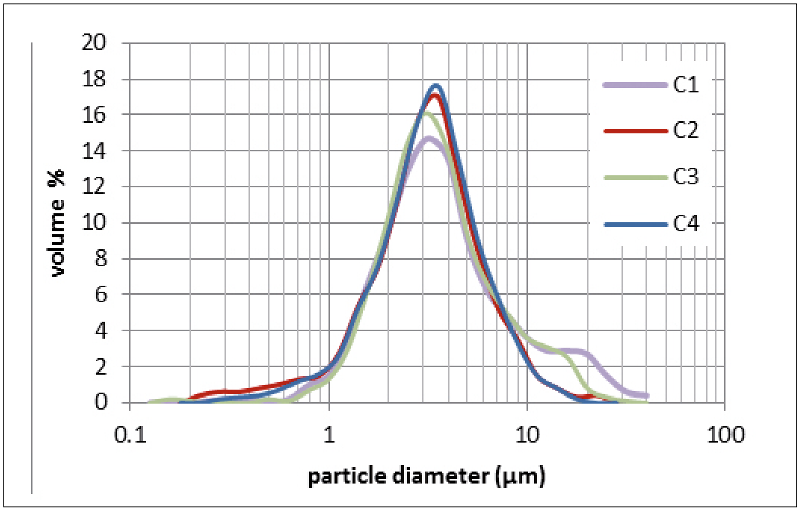

Fig. 1 Calcined alumina particle size distributions (sedigraph)

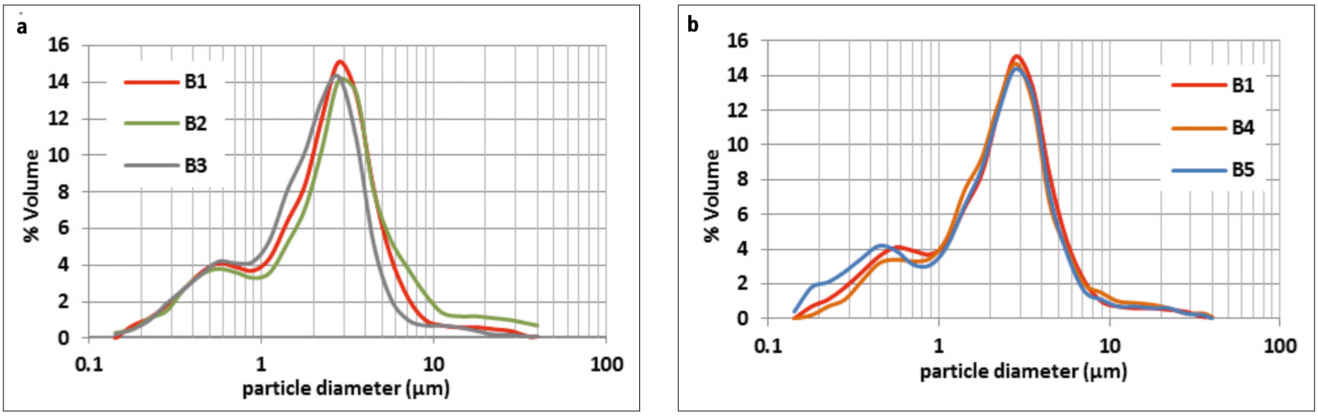

Fig. 2 a–b Bimodal alumina particle size distributions (sedigraph)

3 Experiments

Experiments were conducted on various tabular alumina vibrated low cement castables. The first series consists of analysing the effect of particle size distribution of the 3 µm calcined alumina product in free silica castables (Tab. 2) and with silica castable (Tab. 3). In the second series, the 3 µm calcined alumina has been additivated with various proportions of monomodal reactive alumina to achieve bimodal alumina performance (Tab. 4). The last series consists in analysing the effect of particle size distribution of the bimodal alumina in LCC castable (Tab. 6).

In order to get low water requirement and good compactness, LCC tabular alumina castable formulations have been optimised with Dinger and Funk's packing model with a distribution modulus of 0,27. This modulus value is chosen to achieve a dense structure via vibrating. The ratio of each grade in the castable will depend on the particle size distributions of the aluminas.

The placement properties were studied through vibrating castable measurements in time at constant water content for each series. Flowability was measured by a cone test according to EN ISO 1927-4 norm. The test consists of filling a cone with castable slurry, removing the cone, and measuring the spread diameter after 20 s vibration (average of two opposite diameters). Flow value is calculated as a percentage (spread diameter-initial diameter)/(initial diameter × 100).

The compositions were mixed and tested in a rheometer according to the method developed by R.G. Pilegi, et al. [6]. Torque is measured during the castable mixing before and after water addition at a constant speed (60 rpm). The used apparatus is limited to coarse aggregate size up to 3 mm.

Open porosity and density measurements were performed according to EN 993-1.

Cold flexural strength was measured according to ASTM C1161 on bar samples (150 mm × 25 mm × 25 mm) dried at 110 °C 24 h and fired at different temperature for 5 h.

Refractoriness under load (RUL) was carried out with Netzsch RUL 421E equipment up to 1600 °C under a heating rate of 5 °C/min and compression load of 0,2 MPa, on cylindrical samples pre-fired at 1500 °C for 5 h.

4 Results and discussions

4.1 New calcined alumina with a d_{50} of 3 µm

The particle size distribution curve of this new alumina has been investigated in order to see the influence on the placing properties of low cement vibrating castable (Tab. 2).

Tab. 2 Composition and characteristics of LCC vibrating castables with 3 µm calcined alumina

Mix		**C1**	**C2**	**C3**	**C4**
		Components [%]			
Tabular alumina	0–6 mm	82	82	82	82
Alumina	C1	13			
	C2		13		
	C3			13	
	C4				13
Cement	Secar71	5	5	5	5
Additives	FS60	0,2	0,2	0,2	0,2
Water		5	5	5	5
Flowability [%]		97	129	119	123

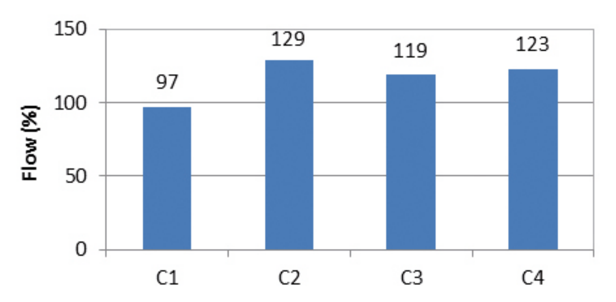

Fig. 3 **Flowability of LCC castable with 3 µm calcined alumina**

Tab. 3 Composition and characteristics of LCC vibrating castables with silica fume

Mix		**C2 +SF**	**B1 + SF**
		Components [%]	
Tabular alumina	0–6 mm	82	82
Calcined alumina	C2	11	
Bimodal alumina	B1		11
Silica fume	MS971	2	2
Cement	Secar71	5	5
Additives	FS20	0,2	0,2
Water		4,4 %	4,4 %
Flowability [%]		**119**	**116**
Density [g·cm^{-3}]	d110	3,13	3,11
	d1500	3,17	3,17
Porosity [%]	Po 110 °C	10,9	10,7
	Po 1500 °C	14,6	14,6
Cold crushing strength [MPa]	CCS 110 °C	67	74
	CCS 1500 °C	182	213

Comparing C1 and C3, the d_{90} parameter is crucial for flowability (Fig. 1 and Fig. 3). Comparing C2 and C4, the presence of fines with a low d_{10} can improve flowability but influence is not as crucial as d_{90}. The C2 curve that combines a narrow distribution for the coarse particles and more fine particles below 1 µm is the most effective to perform a high flowability castable. Calcined aluminas contain sintered agglomerates of individual crystals. And these agglomerates have internal porosity that absorbs water that does not contribute to the flowability of the castable. It means that the agglomerates contribute to increased water demand, or decreased flowability at constant water content. A new continuous grinding device makes it possible to obtain the C2 particle size distribution curve that is nearly ground down to the primary crystal size.

That is why in many applications this kind of alumina can be efficient. To achieve the desired particle packing, it can be combined with silica fume. In this case, it can reach the level of a bimodal alumina, in terms of flowability, water demand and cold physical properties (Tab. 3 and Fig. 4).

In the case of applications where silica fume is prohibited because of negative impact on

Fig. 4 Flowability of silica fume castable with 3 µm calcined alumina and bimodal alumina

Tab. 4 Composition and characteristics of castables with calcined and reactive monomodal aluminas

Mix		B1	C 100/0	C 95/5	C 85/15	C 75/25	C 67/33	C 50/50
		Components [%]						
Tabular alumina	0–6 mm	82	82	82	82	82	82	82
Alumina	C2	–	13	12,3	11	9,8	8,7	6,5
	MR	–	0	0,7	2	3,2	4,3	6,5
	B1	13	–	–	–	–	–	–
Cement	Secar71	5	5	5	5	5	5	5
Additives	FS60	0,2	0,2	0,2	0,2	0,2	0,2	0,2
Water		4,6	4,6	4,6	4,6	4,6	4,6	4,6
Flowability [%]		143	105	124	139	148	152	138
Density [g·cm^{-3}]	110 °C	3,2	3,17	3,17	3,18	3,19	3,19	3,17
	1500 °C	3,07	3,02	3,03	3,04	3,05	3,07	3,07
Porosity [%]	110 °C	12,4	13	12,9	12,6	12,5	12,7	13
	1500 °C	18,2	19,2	19	18,9	18,6	18,2	18
CCS [MPa]	110 °C	88	69	72	81	84	83	87
	1500 °C	166	130	137	144	146	156	160

hot properties, and when a high flowability is required, the comparison to bimodal alumina shows the limit of this calcined product.

In that case, this calcined product can be combined with fine reactive alumina (MR) to achieve the desired particle packing with optimisation of Dinger and Funk model (Tab. 4).

By increasing the rate of reactive alumina up to the range 25–33 %, an optimum of flowability and unfired density is obtained (Fig. 5). Thus, for an appropriate range of reactive alumina addition, it is even possible to get higher flowability than with a bimodal product. The rheology behaviour of the castable during mixing also changes with the addition of reactive alumina. The torque at the turning point and after homogenization is lowered through increasing the rate of reactive alumina.

The density, CCS and CMOR (Tab. 4 and Fig. 6) values can also be increased with the reactive rate and achieve the level of the castable with the bimodal alumina. Yet, the refractoriness under load (Fig. 7 and Tab. 5) shows the limit of the mix calcined alumina and reactive alumina. It is certainly due to the higher soda content of calcined alumina compared to bimodal reactive alumina.

It means that in the case of high temperature performance castable, there is still a need for bimodal reactive aluminas.

4.2 Bimodal aluminas

In order to understand the effect of the particle size distribution shape of bimodal reactive alumina, different co-grindings have been performed (Fig. 2) and compared in castable compositions (Tab. 6). These compositions include aggregates only up to 3 mm, unlike the previous ones that include up to 6 mm. It has been done in order to be able to do torque measurements without

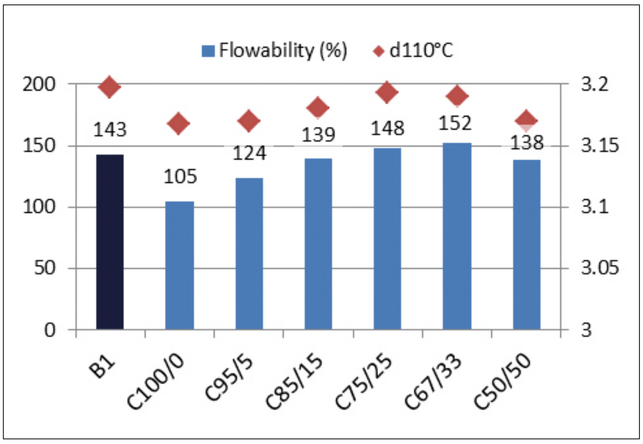

Fig. 5 Flowability and density after drying at 110 °C of LCC castables with different calcined alumina C2/monomodal reactive alumina ratios

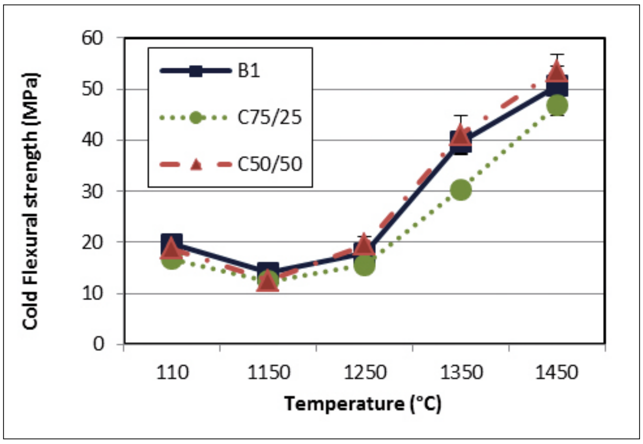

Fig. 6 Cold modulus of rupture of castable at different firing temperatures

damaging the device. It explains why water demand is a little higher for these formulations.

Through comparing B1, B2 and B3, one can clearly see the positive impact of a good top cut for the coarse peak on castable properties. The narrower the basis of the peak, the better the flowability and the unfired density will be (Fig. 8). Meanwhile residual torque after 25 min mixing is lowered and mixing time is shorter to reach the torque maximum peak (Fig. 9).

The effect of the peak of fine particles can be seen through the comparison of B4, B1 and B5 that have the same coarse peak shape but whose amount of very fine particles is gradually increased. It seems that the presence of very fine particles (<0,2 µm) helps to increase flowability and unfired density. It also helps to shorten mixing time and reduce torque during the decreasing phase. No real correlation can be made to the maximum torque peak value.

Beyond the alumina particle size distribution effect on castables, the influence of the dispersant's nature has also been investigated. An Alteo bimodal alumina B1 and another commercially available bimodal alumina BM have been tested in the same conditions with two different dispersive systems: one polycarboxylate based dispersant FS60 and one dispersing alumina. While BM alumina is clearly adapted to the dispersing alumina system, B1 seems more polyvalent and gives slightly better results with FS60. It means that even in optimised configurations, the ranking between two bimodal aluminas may change depending on the type of dispersant used.

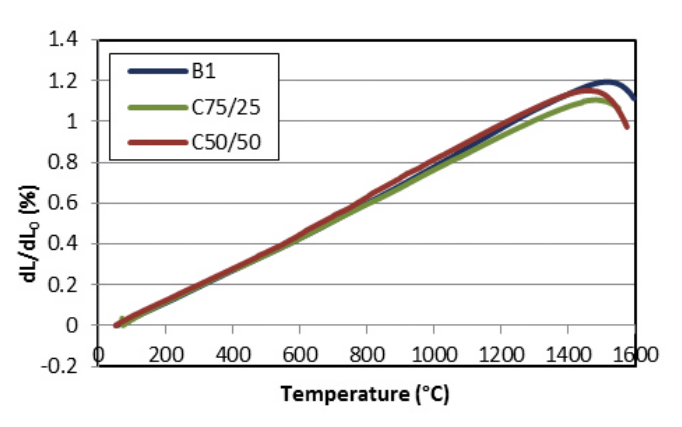

Fig. 7 Refractoriness under load of LCC castable

Tab. 5 Refractoriness under load characteristics

Castable	B1	C 75/25	C 50/50
T 0,5 % [°C]	>1600	>1600	> 600
T (D_{max}) [°C]	1516	1482	1451
dL/L_{max} [%]	1,19	1,12	1,15

Tab. 6 Composition and characteristics of castables with bimodal aluminas

Mix		B1	B2	B3	B4	B5
		std	high sd90	low sd90	low sd10	high sd10
		Components [%]				
Tab. alumina	0–3 mm	82				
B Alumina	$Bi_{i=1\ to\ 5}$	13				
Cement	Secar71	5				
Additives	FS60	0,2				
Water		4,8				
Flowability (%)		122	71	130	93	130
Density [g·cm^{-3}]	d 110 °C	3,13	3,12	3,17	3,11	3,16
	d 1500 °C	3,02	3,01	3.05	3,01	3,03
Porosity [%]	Po 110 °C	15	14,7	14	15,6	14,3
	Po 1500 °C	19,9	20,3	19,4	20,3	19,7

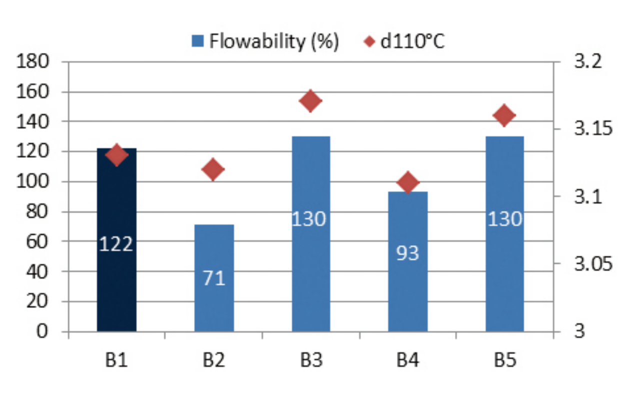

Fig. 8 Flowability and density after drying 110 °C of LCC castables with different bimodal alumina

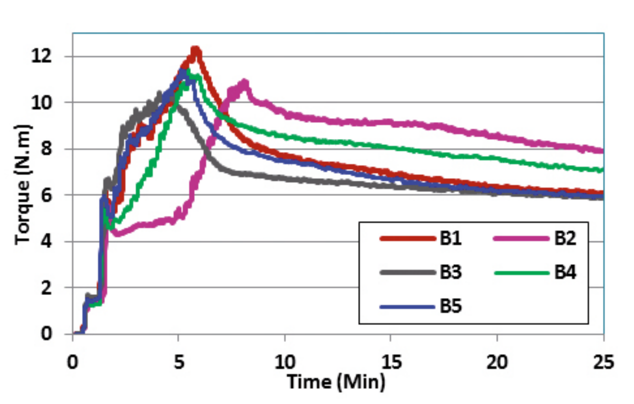

Fig. 9 Mixing torque of castable with different bimodal aluminas

Tab. 7 Composition and characteristics of castables with bimodal aluminas and different dispersants

Mix		**B1-a**	**BM-a**	**B1-b**	**BM-b**
		Components [%]			
Tabular alumina	0–3 mm	82			
Alumina	B1	13		13	
	BM		13		13
Cement	Secar71	5	5	5	5
Additives	FS60	0,2	0,2		
	Dispersing alumina			1,0	1,0
Water		4,8	4,8	4,8	4,8
Flowability [%]		**122**	**99**	**120**	**123**

5 Conclusions

The investigations show that not only the d_{50} of an alumina, but also its particle size distribution curve is fundamental to optimise the rheological properties of alumina based low cement castables. By adjusting the shape of its particle size curve, it presents the possibility using 3 µm calcined alumina in many castable configurations with a suitable flowability. In the case of applications where very low water demand is required, this calcined product can be combined with fine reactive alumina in order to achieve the desired particle packing optimization.

For bimodal reactive alumina, the control of the particle size distribution, with the presence of very fine particles in the first peak and a good top cut for the second peak, makes it possible to increase flowability, lower mixing time and improve physical properties.

Besides the PSD of alumina, the additives also play an important role that will differ from one alumina to another. The nature of the additives has to be adjusted depending on the kind of alumina.

This approach will be further explored in the next studies.

References

[1] Andreasen, A.H.M.: Relation between grain size and interstitial space in products of unconsolidated granules. Kolloid-Zeitschrift **50** (1930) 217–228

[2] Dinger, D.R.; Funk, J.E.: Particle packing II – Review of packing of polydisperse particle systems. Interceram **41** (1992) [2] 95–97

[3] Dinger, D.R.; Funk, J.E.: Particle packing III – Discrete versus continuous particle sizes. Interceram **41** (1992) [5] 332–334

[4] Sarkar, R.; Parija, A.: Effect of alumina fines on high alumina self-flow low cement castables. refractories WORLDFORUM **6** (2014) [1] 73–77

[5] Parr, C.; et al.: Recent advance in refractories aluminate binders and additives for high performance monolithic castable. Irefcon 2008, Kolkata, India

[6] Pileggi, R.G.; et al.: Novel rheometer for refractory castables. Amer. Ceram. Soc. Bull. **79** (2000) [1] 54–58

12TH

IREFCON 18

INDIA INTERNATIONAL
REFRACTORIES CONGRESS

www.irefcon.org

REFRACTORIES SOLUTIONS

THROUGH USER COLLABORATION

7TH TO 9TH MARCH 2018 | VIVANTA BY TAJ, DELHI

REGISTRATIONS OPEN

TECHNICAL SESSIONS

- Coke & Iron Making
- Steel Making
- Secondary Refining
- Flow Control
- Cement & Glass
- Non-ferrous Products
- Petrochemicals
- Monolithic Refractories
- Natural & Synthetic Raw Materials for Refractories
- Nano-engineered Refractories
- Refractory Research & Education
- Refractories Installation & Repairing Techniques

For further details, please contact

The Organising Secretary
12th India International Refactories Congress (IREFCON-2018)
C/o, Indian Refactory Makers Association
5, Lala Lajpat Rai Sarani, Kolkata -700020, INDIA
P: (91) 33 2281 0868, T: (91) 33 2281 4357, E: irmaindia@hotmail.com

IRMA
PARTNERING HEATING SOLUTIONS

Witness a unique platform where the refractory makers from India & worldwide will interact with the refractories producers and users.

DATE
7th - 9th March 2018

VENUE
Vivanta by Taj - Dwarka, New Delhi.

THEME
Refractories Solutions throung User Collaboration

KEYNOTE SPEAKER
Tom Vert, Arcelor Mittal Dafasco, Canada

wishboxindia.com