Upgrading Castable Performance through Matrix Optimization

Xinyu Liu, Gunter Büchel, Andreas Buhr

Abstract

Fine and superfine components, here referred to as matrix, are an important part of refractory castables that determine, besides the flowability, workability and strength, the performance in refractory application. Tailor-made calcined and reactive aluminas, calcium aluminate cement, dispersing additives, Tabular Alumina or other fines can contribute significantly to the improvement of the matrix-performance with respect to low water demand, setting control and strength development. An optimized matrix system, i.e., a Matrix Advantage System (MAS), enables one to get a low-moisture and high strength castable with controllable setting behavior at a water content of 4.6-3.6% for vibrational flow or 4.8% for self-flow properties. A Matrix with high stability can enable, when customized through the newly developed Alcoa Integrated Matrix (AIM), the design of a castable formulation to become even simpler and more robust. AIM can satisfy the workability as required both by vibration and self-flow installations. Substituted by different Al_2O_3-based aggregates (e.g. spinel), the overall performance of castable can be easily steered to meet the specific application requirements.

Key words: castable; performance; matrix optimization; matrix customization

1. Refractory Matrix and Properties of Matrix Raw Materials

1.1 Refractory matrix

A refractory castable is composed of two parts: coarse aggregates and fines. In a recipe, the proportion of aggregates (>45μm) usually constitutes 65-75% of the total. Coarse raw materials for high alumina castables are, for example, Tabular Alumina (T-60/T-64), Magnesium Aluminate Spinel (AR 90, AR 78), fused alumina, bauxite, chamotte, or a combination of them. The quality of those raw materials determines, to a large extent, the characteristics of castables. High purity raw materials such as Tabular Alumina and Magnesium Aluminate Spinel are widely used in the production of porous plugs, well blocks and steel ladle linings.

The matrix of a refractory castable is usually composed of four kinds of raw materials such as calcined or reactive alumina (or SiO_2 fume), calcium aluminate cement, additives (e.g. Dispersing Alumina ADS 1, ADS 3, ADW 1), Tabular Alumina or other fines as shown in Figure 1.

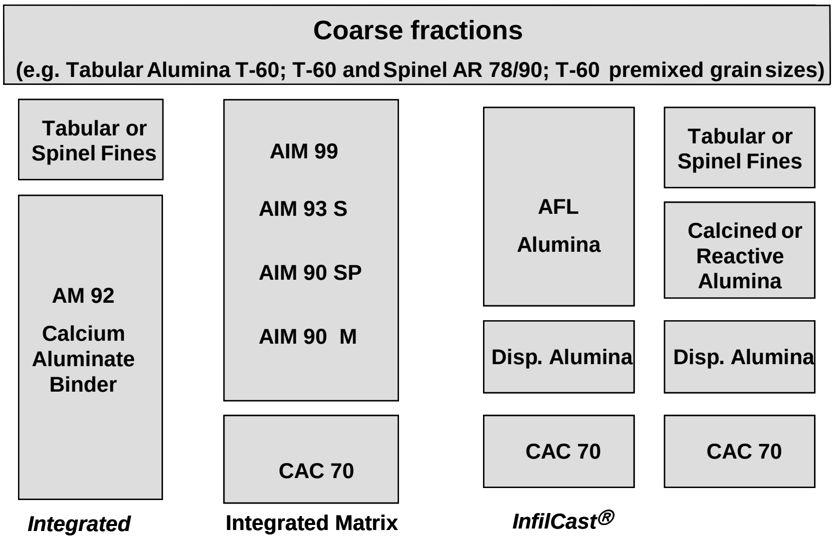

Figure 1. Composition of a refractory matrix

Although a castable formulation only contains 25-35% of matrix components, their behavior strongly determines the castables performance in respect of:

- Flowability (via the water demand)
- Workability (setting time, vibration or self-flow installation)
- Strength (curing strength at room temperature, drying strength at 110 °C, and hot strength)
- Volume stability and wear resistance at high temperatures

1.2 Properties of raw materials for castable matrix

1.2.1 Calcium aluminate cement

Pure calcium aluminate cement with an Al_2O_3 content ranging from 70% to 80% is usually chosen as raw material for high-performance low-cement (LC) or ultra-low-cement cement (ULC) castables. The 80% cement is composed of cement clinker and calcined alumina fines as well as additives and is more frequently used in the production of medium cement to conventional high cement castables, e.g. for robust repair materials for on site installation. The 70% cement is a pure clinker cement and thus has a wider scope of application and, in addition, a higher flexibility in recipe designs. It is widely used in high-performance LC and ULC cement castables.

Cement in castables has the following functions:

- To give the castable a proper curing and drying strength through the hydration of the cement phases
- To provide sufficient time for castable installation
- To form a ceramic bond at high temperature via calcium hexaluminate (CA6) formation

Advances in Alcoa's cement production are reflected in the improvement of the cement consistency and reproducibility of castable performance. CA-14, a 70% alumina cement, is a good example for these positive changes: CA-14 bonded castables require little water, have a high flowability and thus a high strength. Three types of CA-14 cements with controlled setting time are available to better meet different working conditions (S, M and W grade).

Table 1. The setting behavior of 70% Cement (CA-14 W/M/S) in a Nortab testmix (20% cement, 80% Tabular Alumina up to 2mm)

Product	Performance	Final setting (Vicat) with 10% water
CA-14 W (Winter)	Fast setting	170-250 minutes (min/max)
CA-14 M (Medium)	Intermediate setting	250-350 minutes (min/max)
CA-14 S (Summer)	Slow setting	350-480 minutes (min/max)
CA-270	Very slow setting	480 minutes (max) with 9 % water

CA-270 cement, which is also a 70% cement, is specially designed for low moisture castables. It´s mineralogical phase composition is designed for low cement castables with higher strength. Its particle size is even finer and with a bi-modal distribution, thus resulting in castables with a further improved packing density, a reduced water demand, and high flowability and strength.

1.2.2 Calcined and reactive aluminas

In contrary to calcined alumina, reactive aluminas have the following characteristics:

- Small primary crystal size, <1 µm for monomodal aluminas
- Fully ground to eliminate porous agglomerates
- High specific surface area, >1.5m²/g
- Low soda level, typically <0.15%

- In terms of particle size distribution, alumina fines fall into two categories: mono-modal and multi-modal distribution. The multi-modal particle size distribution refers to a distribution which has more than one peak in the functional distribution curve. Multimodal reactive aluminas cover a broad range of the matrix particle size distribution, whereas monomodal aluminas need to be combined with other products to achieve the desired particle packing.

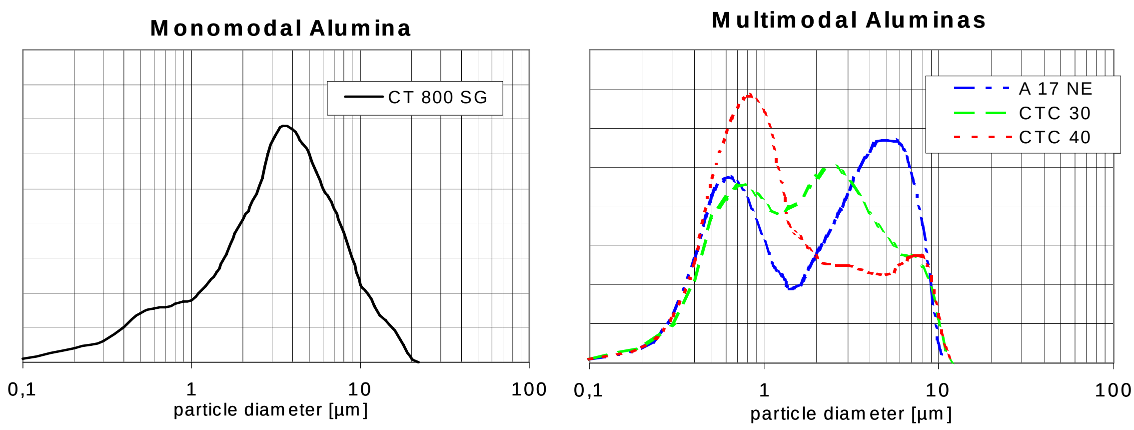

Figure 2: Comparison of the particle size distribution of monomodal CT 800 SG and various multi-modal aluminas

Table 2 shows typical examples of mono-modal and multi-modal calcined and reactive aluminas and their properties.

Table 2 Typical properties of calcined and reactive aluminas

Type	Calcined aluminas		Reactive aluminas					Reactive MA Spinel
Name	CT9FG	CT800SG	CL370C	CTC20	CTC30	CTC50	CT4000SG-R	CTC55
Al_2O_3 (%)	99.5	99.7	99.7	99.7	99.8	99.8	99.8	91.0
Na_2O (%)	0.15	0.12	0.10	0.12	0.08	0.20	0.08	0.10
BET (m^2/g)	0.8	0.9	3.0	2.0	3.8	4.0	6.8	3.8
Particle size D50-Cilas (µm)	5.0	3.6	3.0	2.0	1.8	1.6	0.8	1.7

1.2.3 Dispersing Aluminas

To take full advantage of the castable matrix where the particle size distribution has been optimized for the lowest water demand and desired rheological behavior, it is essential that all the matrix components are homogeneously distributed during mixing with water. Dispersing agents are commonly used to de-agglomerate fine particles. Also used are additives that influence the hydraulic reaction of the cement and steer the setting time of castables. Homogeneous mixing of these agents and additives is inherently difficult, since usual additive concentrations are in the range of 0.01-0.1 wt. %, corresponding to 0.1-1 kg/t of castable mix.

The dispersing function of dispersing agents can be seen during the mixing of high performance castable whose water demand is below 5 %. With water added, the castable initially looks dry. After some mixing, matrix fines start dispersing, and first small crumbs and later larger lumps form. Further mixing results in gradual release of water from the void among the particles as the dispersed reactive alumina replaces the water in the voids, and final mix consistency is obtained after thorough mixing. The total mixing time usually takes 4-6 minutes.
Dispersing Aluminas are innovative products with the function of dispersing matrix fines combined with the function of steering the setting behavior of castables to individual requirements. Two types of Dispersing Aluminas, the retarding type (ADS 1 or ADS 3) and the accelerating type (ADW 1), are used together in a predetermined ratio for a desired setting time. The total amount of Dispersing Aluminas is recommended to be approx. 1 % in weight of the castable. As long as the total amount is kept unchanged, the dispersing capability of Dispersing Aluminas remains stable no matter which type (W or S) or types are used. For castables containing silica fume, Dispersing Aluminas M-ADS 1 and M-ADW 1 have been developed according to the same principle as was applied for developing the original Dispersing Aluminas.

The function of Dispersing Aluminas can be interpreted by the exothermal reaction of a castable as shown in Table 3. The start of the exothermal reaction correlates well to the initial setting time/flow stop of the castable. The exothermal maximum correlates with the strength development/demoulding time. Altering the ratio between retarding and accelerating Dispersing Aluminas can control the setting time of the castable. A higher amount of ADS or M-ADS gives longer setting time, a higher amount of ADW or M-ADW gives shorter setting time. The exothermic reaction shown in figure 3 clearly demonstrates the influence of different ratios of S-type to W-type Dispersing Aluminas on the setting behavior.

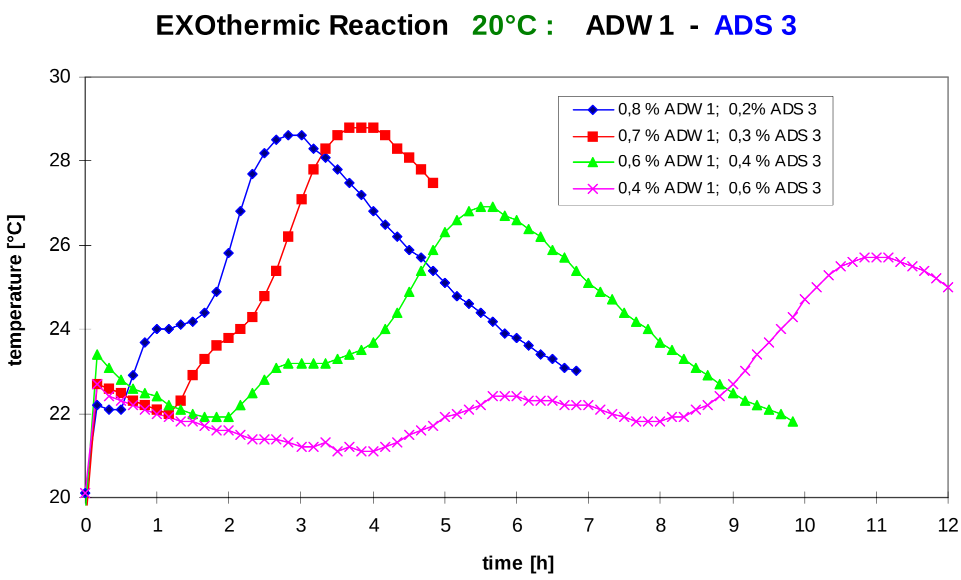

Figure 3: Dispersing Alumina combinations and their influence on castable setting on a Tabular Alumina based self-flowing low cement castable (exothermic reaction)

1.2.4 Tabular Alumina and other fines.

Typical fine sizes used in the matrix are Tabular Alumina 0-0.2mm, 0-0.045 mm and 0-0.02 mm. The particle size distribution of the latter shown in figure 4 indicates a D50 of 3.5 µm and a broad particle size distribution. The broad particle size distribution increases the amount of matrix fines without having too many particles in a narrow size range. Additionally, by using high-fired Tabular Alumina 0-0.020mm as matrix fines, excessive shrinkage during firing can be avoided. The overall effect is to improve flow properties, especially for self-flow castables, and high volume stability during firing.

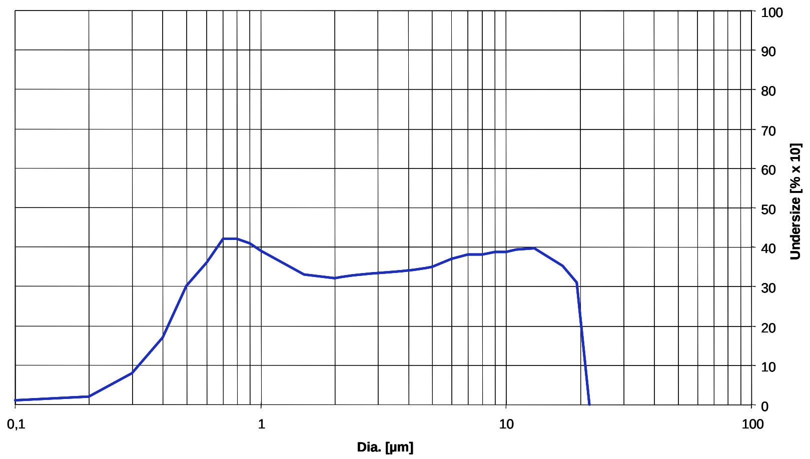

Fig.4 Particle size distribution of Tabular Alumina 0-0.02 mm

2. Effects of Matrix Raw Materials on the Properties of Castables

To show the impact on castable properties such as water demand and strength, tests with different matrix raw materials have been conducted while keeping the chemical composition of the vibration castable constant. The formulation of mixes tested is shown in Table 3.

Table 3 Castable formulation for substitution tests

Raw material	Size or type	Conventional vibration castable	
Tabular Alumina	Aggregates & fines	85	85
Calcium aluminate cement	80% cement	15	--
	70% cement	--	10
Calcined & reactive alumina		--	5
H_2O		7.0 %	4.7 %
Additive	ADW1, ADS1	--	X

2.1 Water demand of castables

Figure 5 shows water demand of five different castables. Replacing 15 % of 80 % CAC by 10 % of the 70 % CA-14 S and matching the missing 5 % Al_2O_3 by introducing the calcined alumina CT 800 SG lowers the water demand immediately down to 6 %. Using CA-270 and the reactive alumina A 17 NE lowers the water demand to 5%. Using optimized reactive aluminas with controlled PSD, such as CTC 30 and CTC 40, gives an improved packing of the mix fines and thereby reduces the water addition further, to 4.8 % with CTC 30 and 4.7 % with CTC 40.

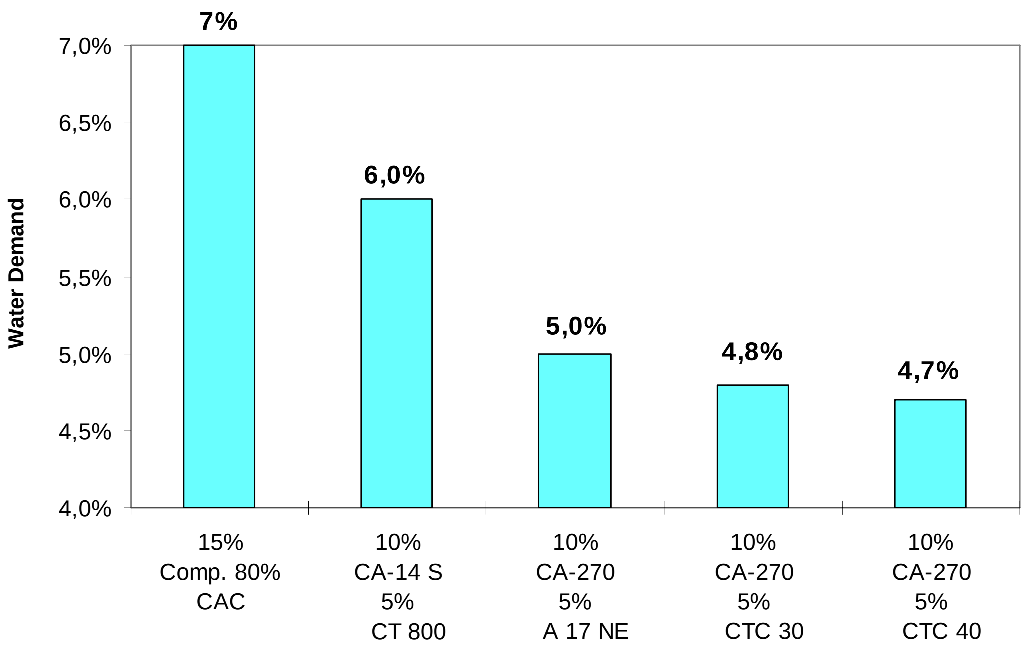

Fig. 4: Water demand of vibration castables with different matrix materials

2.2 The strength of castables

In figure 5 test values for 20°C cured cold crushing strength (CCS) and hot modulus of rupture after 5 h holding time at 1500°C (HMoR) are given. For the cured CCS the highest influence can be observed by the introduction of CA-270, already leading to an increased strength by an improved PSD. The HMoR doubles by using a 70 % cement, but rises even further up with the increasing thermal reactivity of the alumina used. By introducing CTC 30 and CTC 40, the original hot strength (5.8 MPa) is more than tripled to 17.4 MPa.

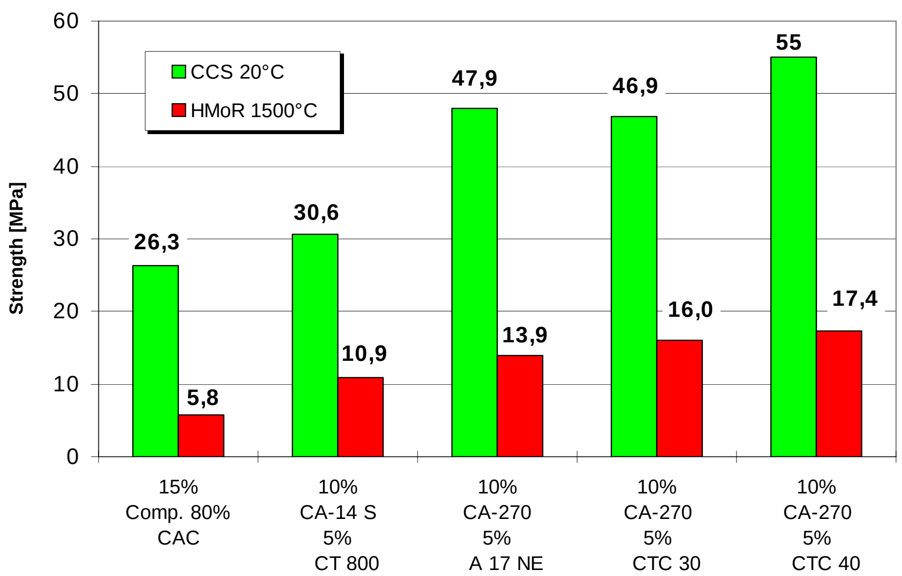

Figure 5: Effects of matrix raw materials on the strength of vibration castables

Generally spoken, by improving the PSD, the water demand of a castable can be reduced drastically, directly resulting in an improved strength even at high temperatures.

3. New trends in castable design: from the Matrix Advantage System (MAS) to Alcoa's Integrated Matrix Products (AIM)

Matrix Advantage System (MAS) is a modular matrix concept, which combines the improved performance of castable formulations with the userfriendliness of individual placement requirements, resulting in a designed matrix for vibration (VIB), self-flow (SFL) and gunning (GUN) placement. The principle of MAS includes:

- A 70% CA cement for VIB and GUN (e.g. CA-14 or CA-270)
- Appropriate calcined and reactive aluminas for desired flow properties (thixotropy, dilatancy) and high strength over the entire temperature range
- Dispersing Aluminas to disperse the matrix and control setting the time (ADS/ADW)
- Optimized particle size distribution to ensure dense packing of the castable

Knowing principally the interaction between the castable design and castable properties, tailor-made castables for any kind of application can be developed.

MAS concept is based on single raw materials, which are necessary to formulate high performance castable refractories. With the introduction of multi-modal reactive aluminas (e.g. CTC-55) and the INFILCAST® technology, which requires the AFL-alumina family, the first steps towards combined matrix products have been made. The second step was the integrated binder AM 92. However, one disadvantage of the AM 92 concept is the lack of flexibility in varying the cement content. The new AIM product family includes fully combined matrix formulations for Tabular Alumina, Spinel, bauxite or Alumino-silicate refractory castables and the added flexibility of using various types and content of 70% alumina cement. Figure 1 lists the new products along with their alumina content and formulation. In the AIM product family, the binders have been omitted to retain flexibility in formulation and avoid ageing problems.

To produce a castable formulation, 20% to 35 % of an AIM product is blended with coarse fractions of the chosen aggregate and one of the hydraulic binders, e.g. calcium aluminate cement or hydratable alumina (Alphabond® 300). AIM contains all of the necessary additives for dispersion and setting control. Due to the intensive pre-homogenization and rigorous quality control of the products, AIM based castable refractories give improved rheological, physical and refractory performance. With AIM only six different components are necessary to achieve high performance castables with cement contents of between 2% and 10 % and water demand down to 4.3%. In addition, the number of components can be reduced still further to three using premixed Tabular Alumina or Spinel based products for the coarse aggregate fraction.

The following AIM products are offered:

		Al_2O_3	
•	**AIM-99**	**99** %	Alumina
•	**AIM-93 S**	**93** %	Alumina + **Spinel**
•	**AIM-90 SP**	**90 %**	Alumina + **Spinel** + **P**ericlase (insitu Spinel)
•	**AIM-90 M**	**90** %	Alumina + **M**icrosilica

Typical product data including chemical and mineralogical composition and fines' top cut is shown in Table 4 .

Table 4: Typical data of AIM products

Chemical Analysis [%]	***AIM-99***	***AIM-93S***	***AIM-90SP***	***AIM-90M***
Al_2O_3	99.5	92.5	88.5	90
MgO		7	9.5	
SiO_2			1.5	9
Na_2O	< 0.3	< 0.3	< 0.3	< 0.3
Fe_2O_3	< 0.1	< 0.15	< 0.15	< 0.1
LOI at 1050 °C [%]	1	1	1	0.5
α-Al_2O_3	XXX	XXX	XXX	XXX
Spinel		XXX	XX	
Periclase			XX	
Microsilica			X	XX
Grain size distribution < 0.045 mm [%]	85	90	95	82

Extensive laboratory investigations with a variety of castable formulations have demonstrated the consistently high performance and flexibility of the AIM product concept. Depending on the sum of AIM product and cement content, the rheology can be defined. All 70% high alumina cements from Alcoa are highly recommended for use with the AIM products. Table 5 shows several examples of AIM-based castables, proving the high flexibility of this system.

The AIM possesses all the functions of the matrix except cement as binder. Compared with a matrix based on individual components, AIM has the following advantages:

- Simplified castable formulation for high production efficiency
- High stability and reproductivity
- Applicable for both vibration and self-flow placement
- Better dispersing effect and controlled setting behavior
- Several AIMs with different properties are available as listed in Table 46, which are pure alumina based (AIM 99), alumina-Spinel (AIM 93 S), alumina-Spinel-Periclase (AIM 90 SP) and alumina-silica based (AIM 90 M).

As examples, 32.5% AIM 93 S is used in castable formulation to achieve good workability for Spinel containing self-flow placements or 25% AIM 93 S for vibration placements. Refractory aggregates can be Tabular Alumina, white fused alumina, MA Spinel, bauxite, or aluminosilicate aggregates to meet specific application requirements at favorable specific refractory consumption. Moreover, cement amount can be changed also to get conventional, low-cement, ultra-low and even non-cement castables in incorporation with the hydratable Al_2O_3 binder Alphabond 300.

Table 5: AIM-based vibration and AIM 93 S based self-flow castables

			VIB	*VIB*	*VIB*	SF	*VIB*	SF	*SF*	*SF*
			AIM 99	*AIM 99*	*AIM 99*	*AIM 93 S*	*AIM 93 S*	*AIM 93 S*	*AIM 90 SP*	*AIM 90 M Mulcoa*
			MCC / 1	*LCC / 1*	*LCC / 2*	*ULCC / 1*	*LCC / 1*	*LCC/1*	*ULCC/1*	*ULCC/1*
Tabular Alumina T-60	Coarse grains	%	70	75	75			50	50	
Spinel AR 90	Coarse grains	%				40	45			
Spinel AR 78	Coarse grains	%				25	25	15	15	
Mulcoa 60	Various sizes	%								56
Alcoa Integrated Matrix	**AIM 99**	%	**20**	**20**	**20**					
	AIM 90 SP	%							**32.5**	
	AIM 93 S	%				**32.5**	**25**	**30**		
	AIM 90 M	%								**32**
CA-cement	**CA-270**	%	**10**	**5**						
	CA 14 M					**2.5**	**5.0**			**2**
	CA-14 S	%			**5**			**5**	**2.5**	
	Total	%	100	100	100	100	100	100	100	100
Mixing water	**SF**	%				**5.0**		**5.3**	**5.0**	**5.0**
	VIB	%	**4.5**	**3.7**	**4.6**		**4.8**			
Flow-values:										
Target > 190 mm VIB	F10	mm	240	200	224		195			
Target > 200 mm SF	F10	mm				247		266	253	255

Main advantages of AIM based castables are:

- High flexibility in castable designs
  > Applicable for vibration and self-flow castables
  > Various cement contents are attainable in the castables
  > Applicable for any refractory aggregates, such as Tabular Alumina, Magnesium Aluminate Spinel and bauxite, etc.
- Good dispersion and water-reduction effects
- High consistency on quality and stability
- Less production cost
- Simplified warehousing

5. Summary

The performance of Al_2O_3-based castables, such as flowability, workability, strength, volume stability and wear resistance is mainly determined by the matrix formulation. Optimizing the packing density of a castable by using multi-modal reactive and Dispersing Aluminas, the water demand can be drastically reduced, resulting in enhanced strength over the entire temperature range.

AIM is the latest advancement in matrix optimization. AIM has altered the recipe designs for castables from multi-components to a formula of aggregates + AIM + cement. By varying the cement type and content castables with various flow properties can be achieved. Different types of aggregates can be chosen to satisfy practical application needs. Simplified and robust recipes have enhanced the stability and reproducibility of castables.

Reference:

1) D. van Garsel, G.W. Kriechbaum, J. V/c Heijden, New Developments of the Improved Durability of Alumina Based Castables, IRE Colloquium, Johannesburg, South Africa, July, 1997
2) G.W. Kriechbaum, J.O. Laurich, D. van Garsel, etc., The Matrix Advantage System, New Raw Materials for Low moisture, Self-leveling Castables, Proceedings of the Unitecr' 97 Congress, New Orleans, USA, Vol.2, P645-655.
3) J.O. Laurich, A. Buhr, Synthetic Alumina Raw Materials – Key Elements for Refractory Innovations, Unitecr´99 Congress, Berlin, Germany, Proc. 348-355