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Benefit of Matrix Alumina and Modern Dispersing Systems in Low Cement Castables

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ABSTRACT

The use of monolithic refractories has spread throughout various industries over the past few decades. Today it is common practice to install monolithics in heavy wear areas. In the past, only refractory bricks were used. Unlike bricks, unshaped products require sintering during operational use to obtain their final properties. Applications outside the iron and steel industry are often referred to as “industrial applications”. Industrial applications also demand improved castable properties such as better chemical stability, mechanical strength and abrasion resistance in intermediate temperature ranges. The service temperatures in industrial applications are often below 1200 °C, so castables do not attain sufficient energy for strong sintering reactions. Matrix properties are important for refractory castables. They determine not only workability and strength, but also performance within an application. By optimising the overall particle size distribution of fine and superfine materials including the binder, better workability can be achieved. In addition, the physical properties of castables can be improved, especially in intermediate temperature ranges. Calcined and reactive aluminas and dispersing additives can also contribute significantly to the improvement of matrix performance with respect to water demand, setting control and strength development.

KEYWORDS

reactive alumina,
dispersing alumina,
low cement castables,
matrix
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1 Introduction

For more than 20 years, low cement castables (LCCs) have been part of the product portfolio of most refractory producers. Many of these formulations have not been updated since they were originally developed, except to change raw materials for economic reasons. It is logical to ask whether there is value in spending R&D resources to improve the current “simple” castable refractories.

The requirements for castables in industrial applications have changed over time. Longer life to achieve better performance to cost ratio is a general demand. Products are required to provide greater ease of installation. Installation of castables sometimes takes place in challenging climatic conditions. Long transportation distances are often involved. Highly skilled staff are not always available for installation. A range of other technical properties are also important:

- easy placement (vib, self-flow, pumping)
- fast wet-out
- controlled and reliable setting
- Tolerance of varying temperatures
- quick de-moulding
- long shelf life (aging stability).

It is therefore worthwhile to take a closer look at the formulations of the existing simple castables to try to achieve better overall performance.

A refractory castable contains both coarse aggregates (particle size >45 µm) and fines. In a recipe, the aggregate proportion usually constitutes 65–75 % of the total castable composition. Examples of coarse raw materials used in castables for industrial applications are: chamotte, bauxite, brown fused alumina, andalusite, or any of them in combination. The quality of the raw materials determines to a large extent the characteristics of the castables [1]. A new sinter aggregate, BSA 96, has been available since 2011 from Almatris for more demanding applications.

The matrix of a deflocculated refractory castable is usually composed of five types of raw material: calcined and/or reactive alumina, SiO₂-fume, calcium aluminate cement, additives for dispersion and set control, and aggregate fines. The calcium alu-

minate cement and aggregate fines (size <45 µm) have comparably high D₅₀ values and broad particle size distributions. They make up the “coarse” part of the matrix, whereas fumed silica and reactive alumina are at the “finer” end with D₅₀ values below 1 µm [2].

Although a castable formulation only contains 25–35 mass-% matrix components, their behaviour strongly determines the castable’s performance with respect to:

- flowability (via water demand)
- workability (wet-out and setting times)
- Strength (curing strength at room temperature, drying strength at 110 °C, and hot strength)
- Volume stability and wear resistance at application temperatures.

The main focus for improvement of industrial application castables is therefore on the composition and properties of the matrix.

2 E-SY 1000 – an engineered reactive alumina

In deflocculated castable formulations based on lower grade alumina aggregates, calcined aluminas are often used in combination with silica fume in order to increase the refractoriness of the matrix by increasing its alumina content [3]. The contribution of

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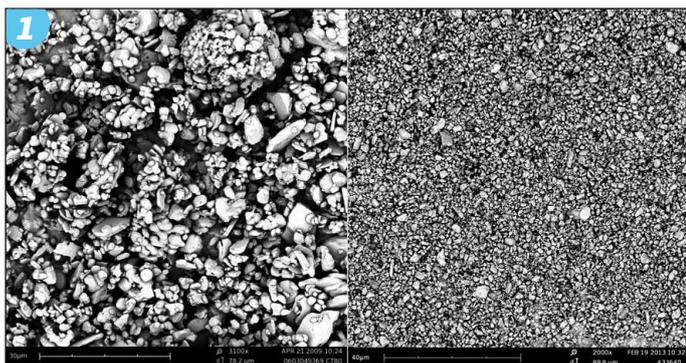


Fig. 1 • Scanning electron microscope (SEM) pictures of calcined (left) and reactive alumina (right)

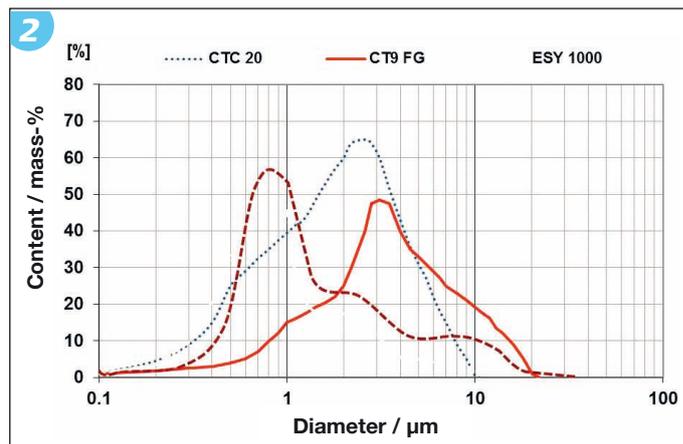


Fig. 2 • Particle size distribution (Cilas) of CT 9 FG calcined alumina and CTC 20 and E-SY 1000 reactive aluminas

alumina to particle packing is not often considered in these cases. This leads to production of materials which do not have optimum properties. Although the D_{50} of finely ground calcined aluminas can come close to that of mid-range reactive aluminas, the products still show significant differences (Fig. 1).

Calcined aluminas contain sintered agglomerates of individual alumina crystals. These agglomerates have internal porosity and absorb water which, as a consequence, is not available to achieve castable flow. This results in increased overall water demand for proper installation consistency. Reactive aluminas, however, are completely ground down to primary (single) crystals. In mono-modal reactive alumina, the average D_{50} particle size is nearly equal to the diameter of the single crystals. The primary crystals are free of pores and do not absorb water.

In terms of particle size distribution, reactive aluminas fall into two categories: mono-modal and multi-modal. Mono-modal aluminas like CTC 20 need to be combined with other products such as silica fume for the ultra-fine part to achieve the desired particle packing. For applications with reducing atmospheres where silica is not desired, this ultra-fine portion can be a super-fine reactive alumina such as RG 4000. Multi-modal particle size distribution refers to a formulation that has more than one peak in its functional distribution curve. E-SY aluminas are specially engineered multimodal reactive aluminas that are produced by co-grinding. This results in higher product homogeneity and gives improved rheological behaviour compared to single component formulations. E-SY 1000 is pure alumina with a bimodal grain size distribution, typical D_{50} of 1.9 μm , and 3.3 m^2/g surface area (BET). Its particle size distribution shows a high proportion of submicron fines

and some coarse material up to 45 microns in size (Fig. 2).

E-SY 1000-containing castables show excellent wetting behaviour and therefore processing can utilise lower energy mixers such as screw types or even simple gravity mixers [4–5].

A BSA 96-based test castable was used for comparison of calcined, reactive and engineered aluminas in order to test their influence on castable properties such as water demand and strength. The chemical composition of the low cement castable was kept constant while adding 45 micron Tabular T60/T64 as a matrix component to CT 9 FG and CTC20 mono-modal alumina. The formulations of the test mixes are shown in Table 1.

Figure 3 shows the water demand of the three different castables at similar flowability. The water requirement of the LCC with 10 mass-% calcined CT 9 FG alumina is already low at 4.7 mass-% due to the dispersing alumina and the use of well-defined 45 micron T60/T64 aggregate fines. 10 mass-% mono-modal reactive CTC 20 alumina reduces the water demand by

0.2 mass-%. With engineered reactive E-SY 1000 alumina the packing of the matrix fines is further improved and this reduces the added water to 4.2 mass-%. A reduction of the water requirement by 0.5 mass-% lowers open porosity of the castable to the range of 1.2–1.7 vol.-%. This improves its mechanical strength and erosion and abrasion resistance.

In industrial applications, process temperatures are often below the point where ceramic sintering starts. Therefore the mechanical resistance of the castables depends mainly on its dense particle packing and the adhesion of ultra-fine particles. The colloidal particles added into silica fume-containing mixes would seem to be sufficient in most cases. However, as shown in Fig. 4, the addition of well-adapted reactive alumina can further optimise such formulations. Cold crushing strength (CCS) is increased by 55 % after pre-firing at 800 °C/5 h when replacing calcined CT 9 FG alumina by engineered reactive E-SY 1000 alumina.

This significant improvement of mechanical strength at intermediate temperatures also

Table 1 • LCCs with silica fume and different matrix aluminas

		Mix 1	Mix 2	Mix 3
		Content / mass-%		
BSA 96	3–6 mm	25	25	25
	1–3 mm	20	20	20
	0.5–1 mm	15	15	15
	0–0.5 mm	15	15	15
T60/T64	–45 μm	7	–	7
Calcined alumina	CT 9 FG	10	–	–
Reactive alumina	E-SY 1000	–	17	–
	CTC 20	–	–	10
Microsilica	955U	3	3	3
Cement	CA-270	5	5	5
Additives	M-ADS 1	0.5	0.5	0.5
	M-ADW 1	0.5	0.5	0.5

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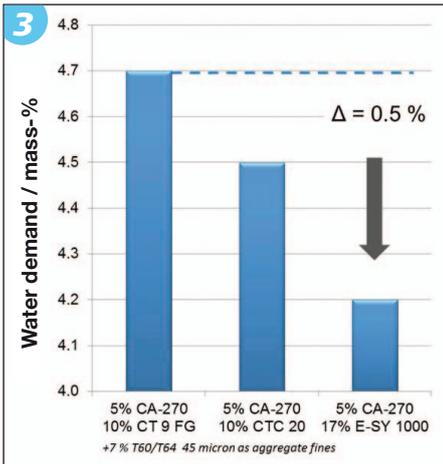


Fig. 3 • Water demand of vibration castables with different matrix aluminas

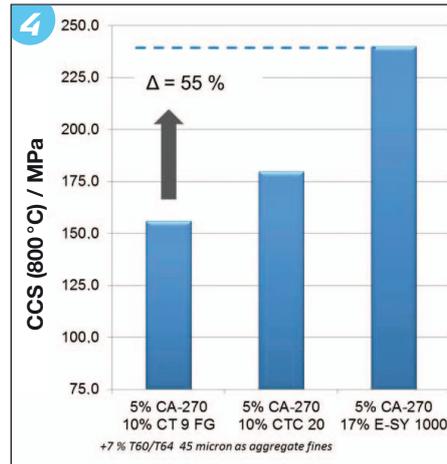


Fig. 4 • Cold crushing strength (CCS) at 800 °C/5 h of vibration castables with different matrix aluminas

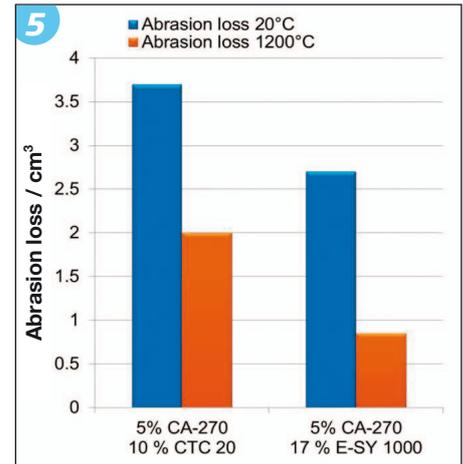


Fig. 5 • Abrasion resistance at room temperature (20 °C) and elevated temperature (1200 °C) of vibration castables with different matrix aluminas according to ASTM C704

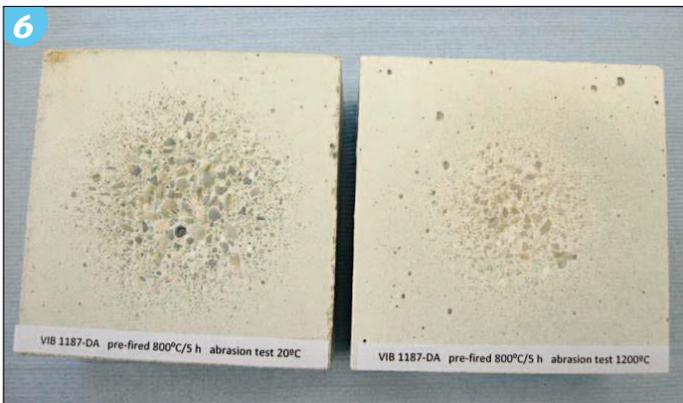


Fig. 6 • Abrasion resistance of BSA 96-based LCC with silica fume and E-SY 1000 reactive alumina; test samples after testing at 20 °C (left) and 1200 °C (right)

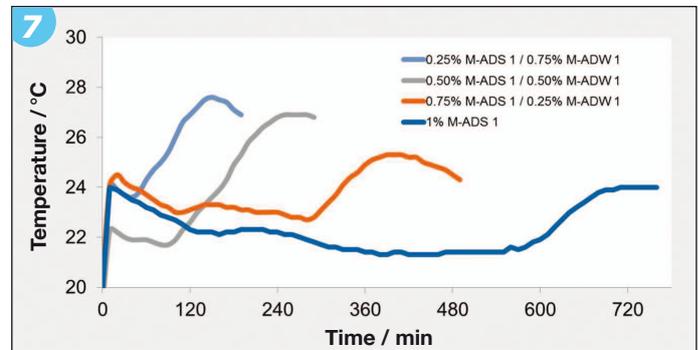


Fig. 7 • Influence of different dispersing alumina combinations on exothermic reaction of a chamotte-based silica fume-containing low cement castable

results in excellent abrasion resistance measured according to ASTM C704. The material loss of E-SY 1000-based castable is below 3 cm³ when tested at room temperature (Fig. 5). To extend the standard, the German Institute for Refractories DIFK, Höhr-Grenzhausen has developed an abrasion test for use at elevated temperatures. After testing at 1200 °C, the weight loss due to abrasion is <1 cm³. This excellent result can be attributed to the good embedding of BSA 96 sintered aggregate in the dense and mechanically stable castable matrix (Fig. 6).

3 Dispersing aluminas AS M-ADS / M-ADW

In low cement castables it is essential that all matrix components be homogeneously distributed during mixing with water. This takes full advantage of optimised particle size distributions to achieve the lowest water demand and exhibit desirable rheological behaviour. Dispersing agents are commonly used to de-agglomerate the fine particles. Further additives influence the hydraulic re-

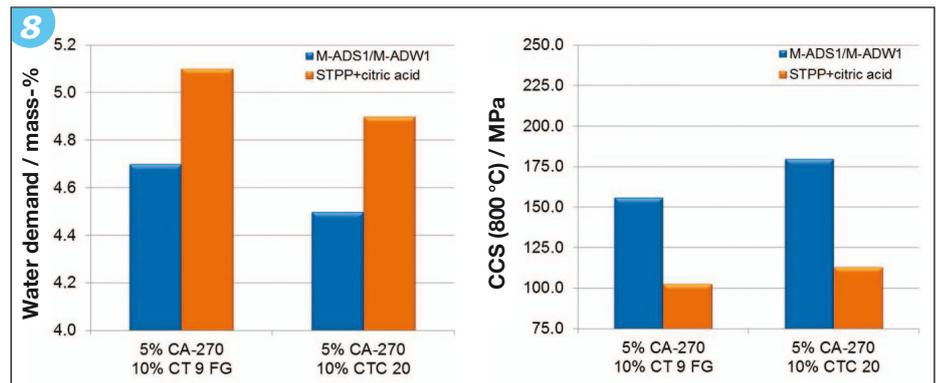


Fig. 8 • Comparison of water demand and CCS of 800 °C/5 h castables dispersed with STPP+citric acid or M-ADS/M-ADW

action of the cement and control the setting time of castables. Phosphates such as sodium-tripolyphosphate (STPP), sodium-hexametaphosphate (SHMP) and mixtures of them are traditional dispersing agents. These are still widely used in low cement castables for intermediate temperature applications. In typical phosphate deflocculated mixes, adjustment of working and setting time is accomplished

by addition of retarders such as citric acid or sodium citrate. The latest generation of dispersing additives are powerful dispersing aluminas. They combine improved dispersing activity with the ability to customise the setting behaviour of castables to individual requirements. For silica fume-containing castables, two types of dispersing aluminas are combined in a predetermined ratio to achieve the de-

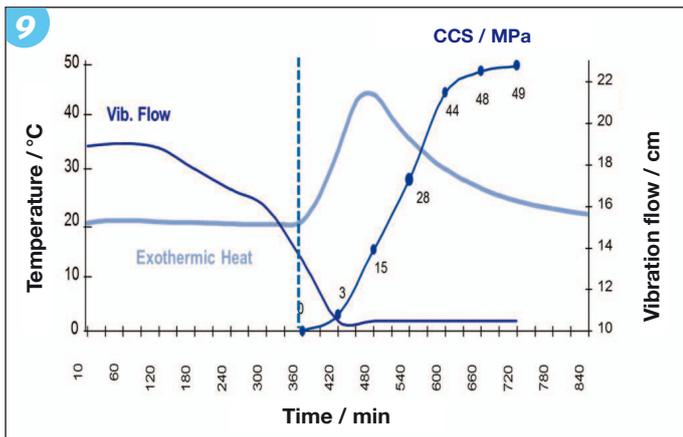


Fig. 9 • Relation of exothermic reaction, flowability, and strength development

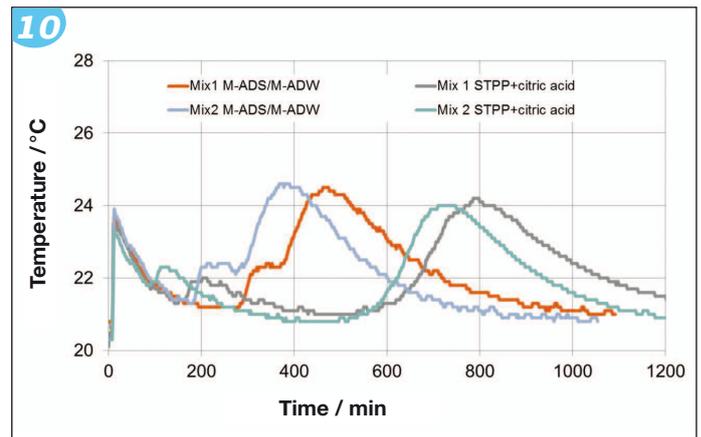


Fig. 10 • Comparison of exothermic reactions of test castables 1 and 2 with STPP + citric acid and dispersing aluminas

sired setting time. They consist of retarding types M-ADS 1 and M-ADS 3 (stronger) and the accelerating type M-ADW 1. The total added dispersing alumina in the castable is recommended to be about 1% by weight. The dispersal effectiveness of aluminas remains the same when different ratios of retarding and accelerating additives are used as long as the total amount is constant (Fig. 7).

When compared to classical phosphate-based deflocculating systems, dispersing aluminas exhibit various advantages:

- lower water demand, and therefore, higher mechanical strength and abrasion resistance
- better control of working time with low impact on the start of setting
- aging resistance for longer shelf life of the castables.

Figure 8 shows a comparison of water demand between dispersing aluminas and the phosphate/citric acid system. Two test castables, the first containing calcined alumina and the other with mono-modal reactive alumina were used, with additions of M-ADS1/M-ADW1 and a mixture containing 0.05 mass-% STPP and 0.01 mass-% citric acid. The water supply was adjusted to reach similar flow values for all samples. For both types of castable, water demand of the phosphate dispersed mix was 0.5% higher than for those with dispersing alumina.

After firing at 800 °C/5 h, castable strength was greater for the dispersing alumina formulations than for the phosphate-containing versions (Fig. 8 b). This strength development is related to hydration of the cement binder. During installation, the strength developed by the castable is important. Sufficient strength development within a reliable time frame is required for proper de-moulding.

For low cement castables, an associated exothermic reaction can be used to analyse the

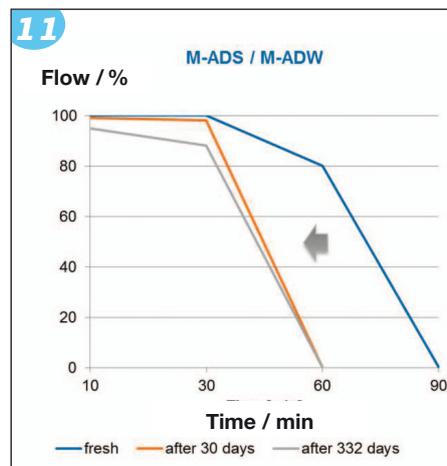


Fig. 11 • Flow behaviour (F30, F60, F90) of a low cement castable with dispersing alumina after storage of 30 and 332 d

setting of the cement. Strength development correlates well with progress toward the exothermal maximum (Fig. 9). When using dispersing aluminas, the flow stop and initial setting time of the castable correlate to the start of the exothermic reaction.

Figure 10 shows the exothermal curves of the two test castables with STPP/citric acid and those with dispersing alumina. The phosphate/citric acid system clearly shows retarding of the cement reaction and delay of strength development. The castables with dispersing alumina reach exothermal maximum after 6–8 h, but take more than 12 h for phosphate-containing mixes. This effect, visible under laboratory conditions at 20 °C, is even further pronounced when working temperatures are lower [6]. It is also important to notice that the phosphate-containing mixes show an initial minor exothermic reaction. This peak correlates with flow stop and an initial slight stiffening of the castable. It is often regarded as the start of cement setting, but is not at all related to the main reaction of the cement which develops

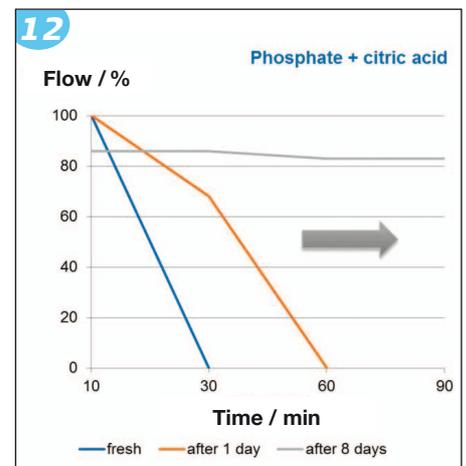


Fig. 12 • Flow behaviour (F30, F60, F90) of a medium cement castable with citric acid after different storage periods [7]

sufficient strength for safe de-moulding. In practice this early stiffening, together with the relatively longer setting time of the phosphate/citric acid castables increases the risk of sagging or damage to the castable lining when forms are removed. By comparison, the improved control of set time enabled by retarding and accelerating dispersing aluminas (Fig. 10) provides greater security for on-site installation and the production of pre-cast shapes.

Another advantage of dispersing aluminas over classical phosphate/citric acid systems is improved aging behaviour of dry mixed castables. Figure 11 shows a chamotte-based low cement castable deflocculated with dispersing aluminas that was tested for its aging behaviour over a period of eleven months. The flow as a percentage of the initial value is plotted for elapsed times of 10, 30 and 60 min after mixing. The end of flow corresponds to the start of strength development as shown in Fig. 9. The fresh castable had an initial set at ~70–80 min which shortened by 30 min after 30 d of storage. In

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the following 10 months no further change of working time/setting characteristics was observed. After 11 months storage the castable still maintained its working time and reliable strength development [6]. The flow behaviour of deflocculated medium cement castable based on brown fused corundum with conventional deflocculating and addition of citric acid is shown in Fig. 12. The fresh castable has a shorter working time of less than 30 min showing that citric acid did not provide as much initial retardation. After storage of one day the flow decay is delayed by around 30 min. After 8 d storage the castable shows a dramatically greater working time of more than 220 min.

Even very low citric acid additions, which are often required to achieve sufficient working time of phosphate-containing castables, can retard the main cement reaction considerably and thus hamper the strength development needed for safe demoulding. This problem can be overcome with the use of dispersing aluminas.

4 Summary

The performance of LC-castables can be adapted to meet more demanding requirements in industrial applications with small modifications in their formulation.

Replacement of calcined aluminas by reactive aluminas such as CTC 20 and E-SY 1000 reduces the demand for mixing water of typical silica fume-containing low cement castables and enhances strength even at intermediate temperatures.

Due to the fast wet-out time of E-SY 1000, on-site water addition can easily be controlled and the risk of overwatering is reduced. Lower energy devices such as screw mixers can be used without negative impact on the homogeneity of the castables.

Castables with an E-SY 1000-containing matrix in combination with BSA 96 sintered aggregate achieve excellent abrasion resistance levels not only at room temperature but also at application temperatures.

With the use of dispersing alumina the water demand of a castable can be significantly reduced when compared to the classical dispersing additive package of phosphate/citric acid (for the same base matrix alumina).

Castables using dispersing aluminas exhibit stable setting behaviour over long storage times. This guarantees reliable installation properties of stockpiled mixes.

The unique combination of retarding and accelerating dispersing aluminas allows full control of the working time of a castable without negative influences on the strength

development needed for successful demoulding.

It is clear that there is still room for improvement of the “simple” castables that are often used in industrial applications.

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