

CASTABLES FOR INDUSTRIAL APPLICATIONS – STILL ROOM FOR IMPROVEMENT!

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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 wear areas where, in the past, only refractory bricks were used. Unlike bricks the unshaped products require sintering in the application to obtain their final properties. Applications outside the iron and steel industry are often referred to as “industrial applications”. The service temperatures in industrial applications are often below 1200°C so castables lack sufficient energy for strong sintering reactions. However, industrial applications also demand improved castable properties such as better chemical stability, mechanical strength or abrasion resistance in the intermediate temperature range. The matrix is an important part of a refractory castable, which determines not only the workability and strength, but also the performance in application. Calcined and reactive aluminas and dispersing additives contribute significantly to the improvement of the matrix performance with respect to water demand, setting control and strength development. By optimising the overall particle size distribution of the fine and superfine materials, including the binder, not only can a better workability be achieved, but also the physical properties, especially in the intermediate temperature range can be improved. This paper reviews the role of matrix alumina in castables for intermediate temperature range applications and provides solutions for further improvement of ordinary low cement castables.

INTRODUCTION

For more than 20 years, low cement castables have been part of the product portfolio of most refractory producers. A lot of these formulations have not been up-dated since they were originally formulated, except maybe for changing raw materials for economic reasons.

We should ask whether it is worth spending R&D resources on this type of “simple” mix?

The requirements for castables in industrial applications have changed over time. Longer life to achieve a best cost to performance ratio is a general demand. Installation of castables sometimes takes place in challenging climatic conditions. Long transportation distances are involved. There are not always highly skilled staff available for installation. Therefore products are required that not only give the best performance in use but also optimisation with regard to ease of installation. This can be summed up as:

- Easy placement (vib, self-flow, pumping)
- fast wet out
- controlled and reliable setting
- tolerance to varying temperatures
- quick de-moulding
- long shelf life (aging stability)

It is therefore worthwhile to take a closer look at the formulations of these “simple” mixes to try to achieve better overall performance. A refractory castable is composed of two parts: coarse aggregates and fines. In a recipe, the aggregate proportion (>45µm) usually constitutes 65-75% of the total. Examples of coarse raw materials used in castables for industrial applications are: cham-

otte, bauxite, brown fused alumina, andalusite or a combination of them. Since 2011 the new Almatiss sinter aggregate BSA 96 has been available for higher demanding applications. The quality of those raw materials determines to a large extent the characteristics of the castables [1].

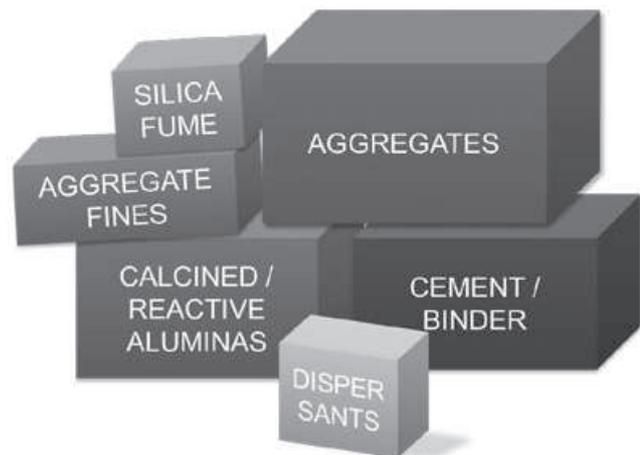


Fig 1: Components of deflocculated low- and ultra-low cement castables

The matrix of a deflocculated refractory castable is usually composed of five types of raw material such as calcined and/or reactive alumina, SiO₂-fume, calcium aluminate cement, additives for dispersion and set-control, and aggregate fines (Fig. 1). The calcium aluminate cement and the aggregate fines <45µm have comparably high D50 values and broad particle size distributions. They can be considered as the “coarse” part of the matrix, whereas fumed silica and reactive alumina are at the “fine” end with D50 values below 1µm [2].

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

- Flowability (via the water demand)
- Workability (wet out time, setting time)
- Strength (curing strength at room temperature, drying strength at 110 °C, and hot strength)
- Volume stability and wear resistance at application temperatures

Therefore the matrix is the focus for improvement of castables for industrial applications.

E-SY 1000 – AN ENGINEERED REACTIVE ALUMINA

In deflocculated castable formulation 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 the alumina content [3]. The contribution of aluminas to an improved particle packing is not often considered in these cases. This leads to materials being produced which do not have optimum properties. Although the D50 of fine ground calcined aluminas can come close to that of mid-range

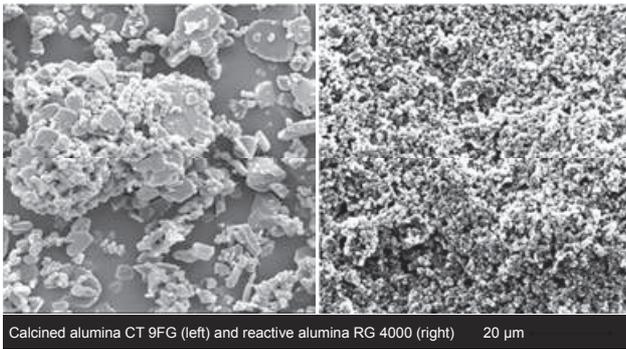


Fig. 2: Scanning electron microscope (SEM) pictures of calcined (left) and reactive alumina (right)

reactive aluminas, the products can still show significant differences (Fig. 2). Calcined aluminas still contain sintered agglomerates of individual alumina crystals. These agglomerates have an internal porosity and absorb water which, as a consequence, is not available to achieve castable flow. The consequence of this is an overall increased water demand for proper installation consistency. Reactive aluminas, however, are completely ground down to primary (single) crystals. Therefore, if it is a mono-modal reactive alumina, the average particle size D50 is nearly equal to the diameter of the single crystals. The primary crystals are free of pores and do not absorb water.

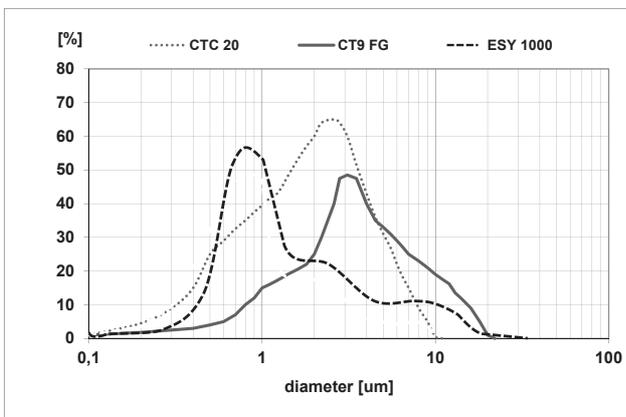


Figure 3: Particle size distribution (Cilas) of calcined alumina CT 9 FG and reactive aluminas CTC 20 and E-SY 1000

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. The multi-modal particle size distribution refers to a distribution which has more than one peak in the functional distribution curve. The E-SY aluminas are specially engineered multimodal reactive aluminas which are produced by co-grinding. This results in higher product homogeneity and gives improved rheological behaviour when compared to single component formulations. E-SY 1000 is pure alumina and characterised by a bimodal grain size distribution with a typical D50 of 1.9 μm, and surface area (BET) of 3.3 m²/g. The particle size distribution shows a high content of submicron fines and some coarse material up to 45 microns (Fig. 3).

E-SY 1000 containing castables show excellent wetting behaviour and can therefore utilise lower energy mixers such as screw mixers 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 by adding Tabular T60/T64 45 microns as matrix component to the mono-modal aluminas CT 9 FG and CTC 20. The formulations of the test mixes are shown in Table 1.

Table 1: LCCs with silica fume and different matrix aluminas

		1	2	3
		%	%	%
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	-45MY	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

Figure 4 shows the water demand of the three different castables at similar flowability. The water demand of the LCC with 10% calcined alumina CT 9 FG is already low at 4.7 % due to the use of dispersing alumina and the use of well-defined aggregate fine T60/T64 -45 micron. Replacing CT 9 FG by 10% mono-modal reactive alumina CTC 20 reduces the water demand by 0.2%. When using the engineered reactive alumina E-SY 1000 the packing of the matrix fines is further improved and this reduces the water addition down to 4.2 %. A reduction of the water addition by 0.5 % means a reduction in open porosity in the range of 1.2 – 1.7 vol.%. This improves the mechanical strength and the erosion and abrasion resistance of the castable.

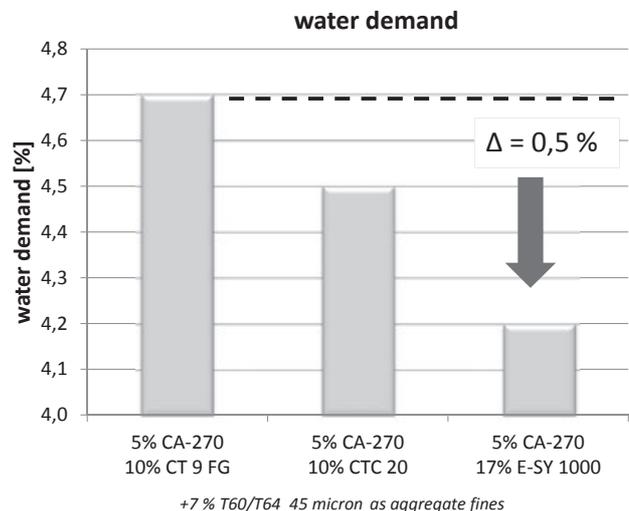


Fig. 4: Water demand of vibration castables with different matrix aluminas

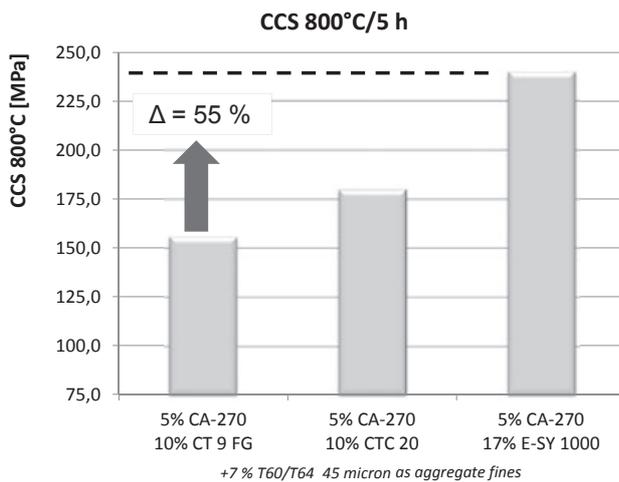


Fig. 5: Cold crushing strength (CCS) at 800°C/5h of vibration castables with different matrix aluminas

In industrial applications the process temperatures are often below the temperatures where ceramic sintering starts. Therefore the mechanical resistance of the castables depends mainly on a dense particle packing and the adhesion of the ultra-fine particles. For silica fume containing mixes one would assume that the amount of colloidal particles introduced should be sufficient. However, as shown in fig. 5 the addition of a well-adapted reactive alumina can further optimise such formulations. The cold crushing strength (CCS) after pre-firing 800°C/5h is increased by 55% when replacing calcined alumina CT 9 FG by the engineered reactive alumina E-SY 1000.

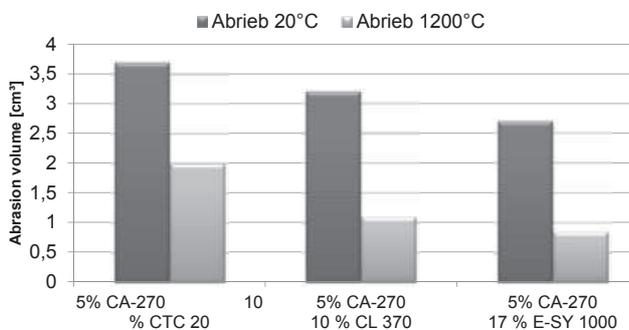


Fig. 6: Abrasion resistance according to ASTM C 704 at room temperature (20°C) and elevated temperature (1200°C) of vibration castables with different matrix aluminas

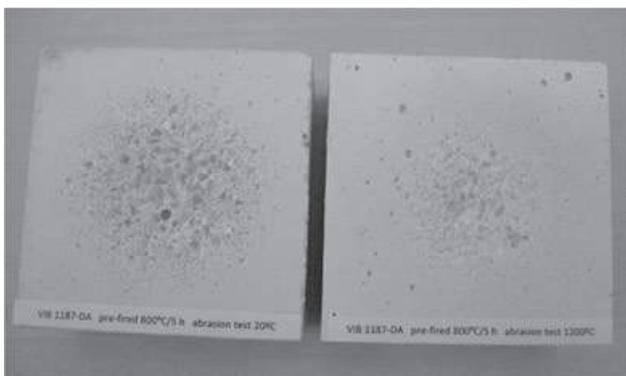


Fig. 7: Abrasion resistance of LCC based on BSA 96 with silica fume and E-SY 1000 reactive alumina; test samples after testing at 20°C (left) and 1200°C (right).

This significantly improved mechanical strength at intermediate temperatures also results in an excellent abrasion resistance acc. ASTM C 704. The material loss of the E-SY 1000 based castable is below 3 cm³ when tested at room temperature (Fig. 6). In accordance with the standard, the German Institute for Refractories DIFK, Höhr-Grenzhausen has developed an abrasion test which is conducted at elevated temperatures. When testing at 1200°C the weight loss due to abrasion is even less than 1cm³. This excellent result can also be attributed to the good embedding of the sintered aggregate BSA 96 in the dense and mechanically stable matrix (Fig. 7).

DISPERSING ALUMINAS M-ADS / M-ADW

In low cement castables it is essential that all the matrix components are homogeneously distributed during mixing with water in order to take full advantage of the optimised particle size distribution and achieve the lowest water demand and desired rheological behaviour. Dispersing agents are commonly used to de-agglomerate the fine particles. In addition further additives are used which influence the hydraulic reaction of the cement and steer the setting time of castables.

Traditional dispersing agents are phosphates such as sodium-tripolyphosphate (STPP), sodium-hexametaphosphate (SHMP) and mixtures of them. These are still widely used in low cement castables for intermediate temperature applications. In such phosphate deflocculated mixes the adjustment of working time and setting time is done by the addition of retarders such as citric acid or sodium citrate.

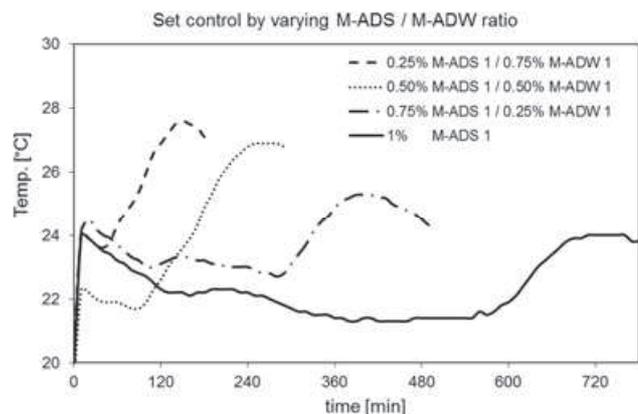


Figure 8: Dispersing Alumina combinations and their influence on castable setting. Exothermic reaction of a chamotte based low cement castable (silica fume containing)

Dispersing aluminas are powerful dispersing additives of the latest generation. They combine improved dispersing activity with the function of steering the setting behaviour of castables to individual requirements. For silica fume containing castables, two types of dispersing aluminas, the retarding types M-ADS 1 and M-ADS 3 (stronger retarding) and the accelerating type (M-ADW 1), are used together in a predetermined ratio for a desired setting time. The total amount of dispersing aluminas is recommended to be about 1% by weight in the castable. When keeping the total amount unchanged, the dispersing capability of dispersing aluminas remains stable no matter which ratio of S/W is used (Fig. 8). When compared to the classical phosphate-based deflocculating systems the dispersing aluminas exhibit various advantages:

- Lower water demand and therefore higher mechanical strength and abrasion resistance
- Control of working time with low impact on the start of setting
- Aging resistance – longer shelf life of the castables

Fig. 9 shows a comparison of dispersing aluminas and the phosphate/citric acid system. The test castables 1 (calcined alumina) and 2 (mono-modal reactive alumina) were modified by replacing M-ADS1 / M-ADW1 by a mixture of 0.05 % STPP and 0.01 % citric acid. The water demand was adjusted to reach similar flow values as for the initial castables. In both cases the water demand of the phosphate dispersed mix was 0.5% higher than for the mix containing dispersing aluminas. Accordingly, the strength values after firing at 800°C/5h are lower for the phosphate containing mixes when compared to the original formulations.

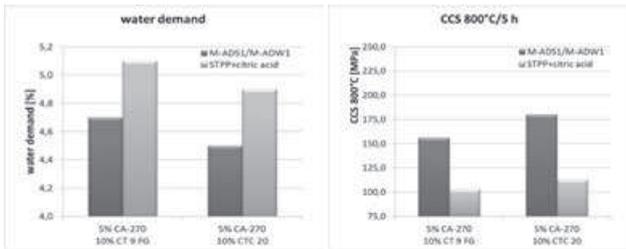


Fig. 9: Comparison of water demand and CCS 800°C/5h of castables dispersed with STPP+citric acid or M-ADS/M-ADW

During installation the strength development of the castable is important once the material is cast into the former. For de-moulding sufficient strength development within a reliable time frame is required. This strength development is related to the hydration of the cement binder. For low cement castables the exothermic reaction can be used to record the setting of the cement. The strength development correlates well with the exothermal maximum (Fig. 10). When using dispersing aluminas, the flow stop and initial setting time of the castable correlate to the start of the exothermal reaction.

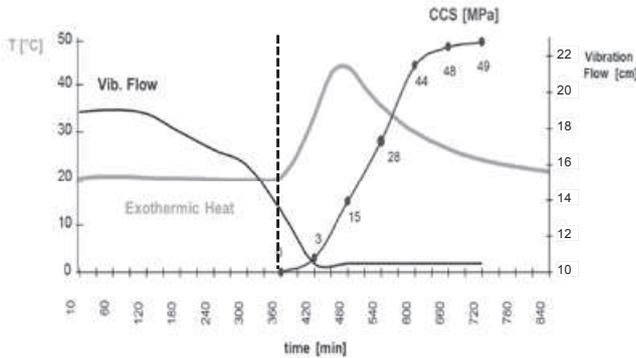


Fig. 10: Relation of exothermic reaction, flowability, and strength development

Fig. 11 shows the exothermal curves of test castable 1 and 2 with STPP/citric acid and dispersing alumina. The retardation of the cement reaction and accordingly the strength development by the phosphate/citric acid system is obvious. Whereas the castables with dispersing alumina addition reach EXO max after 6-8 h it takes more than 12h for the phosphate containing test mixes. This effect, visible under laboratory conditions at 20°C is even further pronounced when working temperatures are lower [6]. It is also important that the phosphate-containing mixes show an initial minor exothermic reaction. This peak correlates with the flow stop and slight stiffening of the castable. It is often translated as start of the cement setting, but it is not at all related to the main reaction of the cement which develops sufficient strength for safe de-moulding. In practice the early stiffening, together with the

comparably long setting time of the phosphate/citric acid castables increase the risk of sagging or damage to the lining when removing the formers. On the contrary, the control of the set-time by varying ratios of retarding and accelerating dispersing aluminas (Fig. 8) provides the desired security for on-site installations or pre-cast shapes.

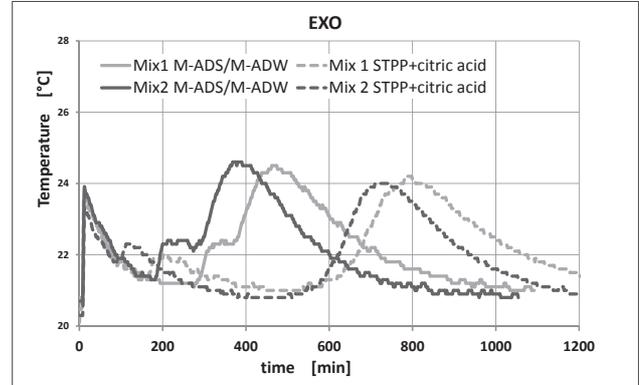


Fig. 11: Comparison of exothermic reactions of test castables 1 and 2 with STPP + citric acid and dispersing aluminas

Another advantage of dispersing aluminas over classical phosphate/citric acid systems is the improved aging behaviour of dry mixed castables. Fig. 12 shows a chamotte based low cement castable deflocculated with dispersing aluminas which was tested for its aging behaviour for a period of eleven months. F10/F30/F60 corresponds to the flow values at 10/30/60 min after mixing and are expressed as a percentage of the initial flow value. As shown in figure 10 the end of flow corresponds to the start of strength development. The fresh castable had an initial set at ~70-80 min which was shortened by 30 min after 30 days of storage. In the following ten months no further change of working time / setting characteristics was observed. After 11 months storage the castable still had its initial working time and a reliable strength development [6]. The flowability of a deflocculated medium cement castable based on brown fused corundum with conventional deflocculating system and addition of citric acid is shown in fig. 13. The fresh castable shows a comparably short working time of less than 30 min although citric acid was added for retardation. After storage for 1 day the flow decay is already retarded by around 30 min. After 8 days storage the castable has changed dramatically showing a working time of more than 220 minutes.

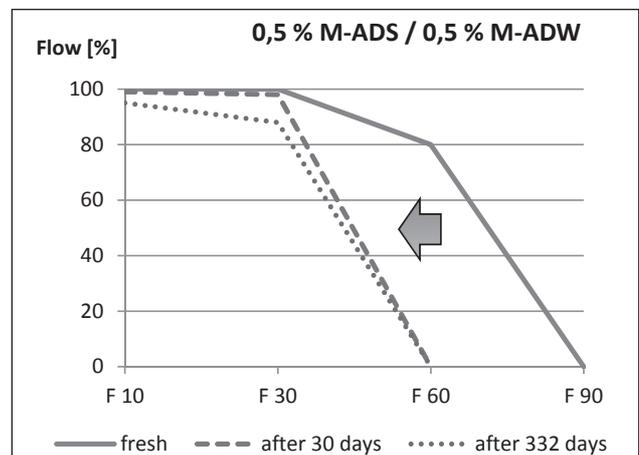


Fig. 12: Flow behaviour (F30, F60, F90) of a low cement castable with dispersing alumina after storage of 30 and 332 days

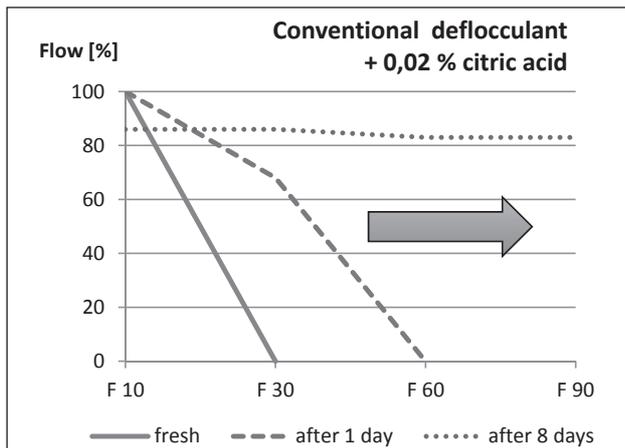


Fig. 13: Flow behaviour (F30, F60, F90) of a medium cement castable with citric acid after different storage periods [7]

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 de-moulding. Such problems can be overcome with the use of dispersing aluminas.

SUMMARY

With small recipe modifications the performance of LC-castables can be adapted to the increasing requirements in industrial applications.

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

Due to the fast wet-out time of E-SY 1000, the water addition on-site can easily be controlled and the risk of overwatering is reduced. The use of lower energy mixers such as screw mixers has no negative impact on the homogeneity of the castable.

Castables with an E-SY 1000 containing matrix in combination with the sintered aggregate BSA 96 achieve excellent abrasion re-

sistance levels not only at room temperature but also at application temperatures.

With the use of dispersing alumina the water demand of a castable -independently of the matrix alumina- can be significantly reduced when compared to the classical dispersing additive package of phosphate/citric acid.

Castables using dispersing aluminas exhibit a stable setting behaviour over a long storage time. This guarantees reliable installation properties of the mixes.

The unique combination of retarding and accelerating dispersing aluminas allows the control of the working time of a castable without negative influence on the strength development for de-moulding.

It was shown, that there is still room for improvement of "simple" castables which are often used in industrial applications

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