

THE VALUE OF ADDITIVE SYSTEMS IN SILICA FUME CASTABLES

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INTRODUCTION

The use of fine matrix fillers such as silica fume and reactive alumina in LC- and ULC-castables requires the addition of additives for dispersion and for adjustment of working time during installation. The choice of the additive has a significant influence on the flow properties, working and setting time and also the strength development of the castable.

This paper discusses extended test series performed with different additive systems in silica fume containing castables and highlights their influence on workability and setting behaviour. The results of short term aging tests of dry mixed castables with different additive systems are also discussed.

Dispersing aluminas

Dispersing aluminas are dispersing agents, designed as pre-mixes, which allow easy dosage and homogenisation. The main functions of the dispersing aluminas are described by Kockegey-Lorenz et al. [1]. For silica fume containing systems M-ADS and M-ADW are used (table 1).

Tab. 1: Typical product data – dispersing aluminas for silica fume containing castables.

Product	M-ADS 1	M-ADS 3	M-ADW 1
Effect	Retarding	Strong retarding	Accelerating
Chemical Composition [%]			
Al <sub>2</sub> O <sub>3</sub>	91	95	96
Na <sub>2</sub> O	1.40	1.40	0.10
B <sub>2</sub> O <sub>3</sub>	1.30	2.50	0.55
CaO	0.02	0.02	0.02

In addition to their dispersion function, the setting behaviour can be steered in a very controlled way by combining the retarding M-ADS and the accelerating M-ADW. The recommended total amount is about 1% for low cement and 0.7% for ultra-low cement castables. By keeping the total amount unchanged, the rheological performance of dispersing aluminas remains stable no matter which ratio of S/W is used [2]. Figure 1 demonstrates the set control by varying the M-ADS 1 / M-ADW 1 ratio in a low cement castable with 5% silica fume.

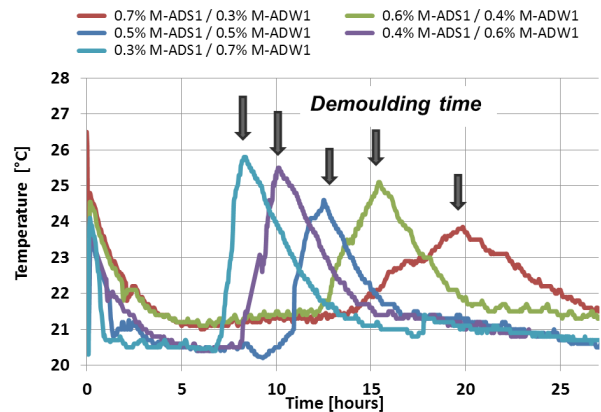


Fig. 1: Dispersing Alumina combinations and their influence on castable setting. Exothermic reaction of a low cement castable with 5% silica fume.

EXPERIMENTAL

Test castables

Two low cement vibration castables with 5% (VIB 5M) and 3% (VIB 3M) of a 94% grade silica fume were selected for the test series. In addition to dispersing aluminas, sodium-tripolyphosphate (STPP) and sodium-hexametaphosphate (SHMP) were also chosen, as they are still widely used as additives in silica fume containing castables. For the adjustment of working and setting time, citric acid was added. Test mix compositions and test results for selected additive dosages are given in table 2.

Tab. 2: Test mix compositions and test results of VIB 5M containing 5% silica fume.

Mix		VIB 5M DA	VIB 5M STPP	VIB 5M STPP/CA	VIB 5M SHMP	VIB 5M SHMP/CA
Components [%]						
T60/T64	up to 6 mm	82	82	82	82	82
Alumina	CT9 FG	8	8	8	8	8
Silica fume	94% SiO <sub>2</sub>	5	5	5	5	5
Cement	CA-14 M	5	5	5	5	5
Additives	M-ADS1	0.4	-	-	-	-
	M-ADW1	0.6	-	-	-	-
	STPP	-	0.1	0.1	-	-
	SHMP	-	-	-	0.05	0.05
	Citric acid	-	-	0.03	-	0.03
H <sub>2</sub> O		4.5	5.0	5.0	5.0	5.0
VIB-Flow	10 min [cm]	22.5	22.7	23.0	23.8	23.0
	30 min [cm]	23.0	17.8	23.5	23.5	23.3
	60 min [cm]	21.8	10.0	23.0	23.0	23.0
EXO	Start 1	66'/21.8°C	n.d.	n.d.	n.d.	n.d.
	Start 2	8.1h/20.6°C	4.3h/20.8°C	9.8h/20.8°C	6.0h/20.9°C	25.0h/20.6°C
	Max	10.1h/25.5°C	6.2h/22.4°C	13.0h/22.9°C	8.9h/23.2°C	30.2h/22.8°C
CCS	20°C / 24 h [MPa]	24	29	26	34	14
C MoR	20°C / 24 h [MPa]	5	4	5	4	3

In addition, some tests were done with castables containing only 3% instead of 5% silica fume. The amount of tabular -45MY Li was then increased by 2%.

The castable components were dry mixed in a Hobart mixer type A200 at speed 1 for one minute and for another four minutes after the addition of water. The flow properties after 10, 30, and 60

minutes were measured by the cone test. The setting behaviour was determined by the exothermal method (EXO) and partially by measuring the ultrasonic velocity (US). Both methods and terminology were described in detail by Gierisch et al. [3]. Test bars were prepared and tested according to the European standard DIN-ISO 1927 part 5 and 6. Cold crushing strength (CCS) and cold modulus of rupture (CMoR) were measured after 24 hour curing at 20°C.

For the investigation of the storage stability, 5 kg batches of dry mixed castables were used. Selected mixes were stored in an open bucket in a climate cabinet at 20°C and 65% relative humidity for 1, 7, and 14 days. The setting behaviour (EXO) was tested for fresh and aged test mixes. The cement hydration with silica fume, phosphate, and citric acid was investigated with a calorimeter, (designed at the University of Erlangen), at a consistent temperature of 23°C ± 0.1°C. The calorimetric test method is described in detail by Kuzel [4].

### Determination of additive dosage

Additive and water additions were adjusted to comparable vibration flow at lowest possible water addition. Focus was not only on flow after 10 and 30 minutes, but also after 60 minutes, to ensure a working time which is sufficiently long for on-site installations. For the dispersing alumina different M-ADS 1 / M-ADW 1 ratios were tested. For the phosphates two series of tests were performed. Firstly, different phosphate additions were tested at a fixed citric acid addition of 0.03%, and in a second test the citric acid dosage was varied while keeping the phosphate content constant. Results for VIB 5M are shown in figures 2 – 6. The time of EXO Max is also given in the figures. Arrows are indicating the mixes shown in table 2.

When using dispersing aluminas M-ADS 1 and M-ADW 1 stable flow properties are achieved for both test castables at a low water addition of 4.5%. Only at a high M-ADW 1 content does flow decay occur at 60 minutes due to an early setting start. By the adjustment of the M-ADS/W ratio the de-moulding time (EXO Max) is steered in the range of 8.3 – 19.8 hours for VIB 5M and 4.4 – 10.4 hours for VIB 3M. If longer working and setting times are required, the replacement of M-ADS 1 by the stronger retarding M-ADS 3 enables further extension without risking ultra-long or never setting times. For the strength tests a dispersing alumina ratio of 0.4% M-ADS 1 and 0.6% M-ADW 1 was selected.

The test castables containing phosphate additives generally require a higher water demand of 5% when compared to M-ADS/W (4.5%). The 0.5% higher water addition which is required for the phosphate dispersed mix might result in lower strength values after firing at 800°C/5h when compared to the dispersing alumina system as reported by Schnabel et al. [2].

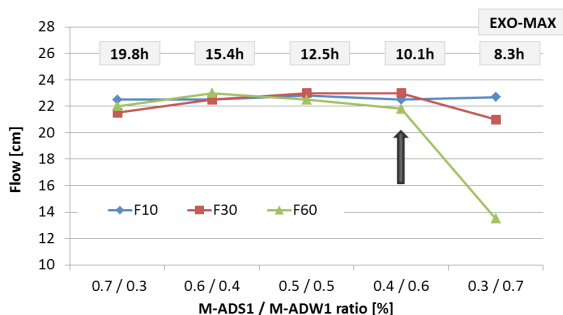


Fig. 2: VIB 5M with different M-ADS/W ratios.

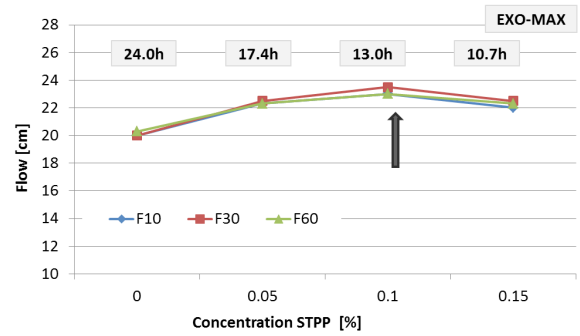


Fig. 3: VIB 5M with 0.03% citric acid and varying STPP addition.

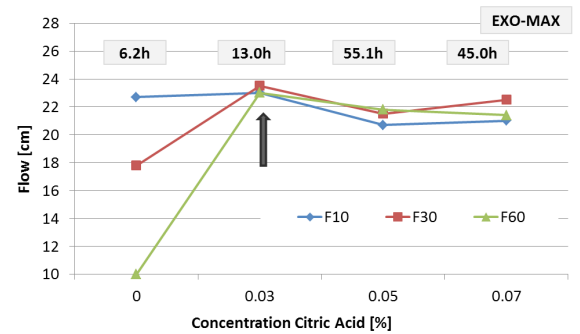


Fig. 4: VIB 5M with 0.1% STPP and varying citric acid addition.

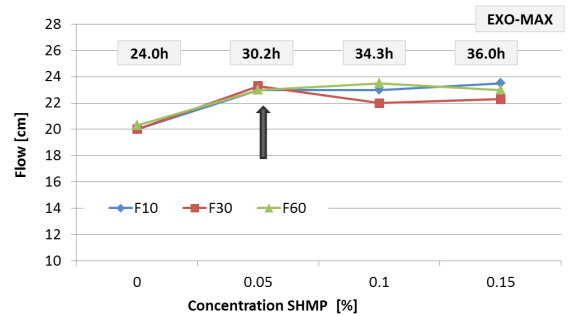


Fig. 5: VIB 5M with 0.03% citric acid and varying SHMP addition.

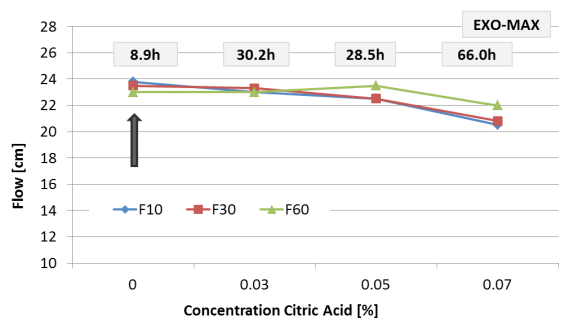


Fig. 6: VIB 5M with 0.05% SHMP and varying citric acid addition.

VIB 5M dispersed with STPP shows an acceleration of the cement hydration with increasing amounts of STPP (figure 3). Without addition of citric acid and 0.1% STPP in the mix, flow decay already occurs after 30 minutes and there is no flow at 60 minutes. By the addition of citric acid flow up to 60 minutes can be achieved. However, the cement hydration is very sensitive to the amount of citric acid as can be seen from the EXO Max times in figure 4. EXO Max increases from 13 hours at 0.03% to about 50 hours at 0.05 - 0.07% citric acid. Slight over-dosages of citric acid in practice would result in an increasingly retarded cement reaction and delayed strength development.

Contrary to STPP, SHMP acts as a retarder in VIB 5M (figure 5). Good flow properties are achieved at a dosage level of 0.05% SHMP even without the addition of citric acid (figure 6). However, when citric acid is added for the extension of working and setting time, EXO Max becomes significantly longer (30 instead of 9 hours with addition of 0.03% citric acid and even 66 hours at 0.07% citric acid).

Experiments with polyphosphates are not part of this paper, but were also performed in extended test series. They showed a similar trend as SHMP. In general all the phosphate systems in this work showed a high sensitivity for citric acid additions which are often applied in practice to steer the working time of the castables. Late cement hydration and strength development are disadvantages.

### Castable setting and strength development

After placing a castable into a mould or a former, the process of strength development is of high importance. Within a specific time period, sufficient strength has to be developed for de-moulding and further processing.

VIB 5M-DA shows good workability over a period of more than 1 hour and achieves de-moulding strength (EXO Max) relatively shortly after the end of working time. EXO Max occurs after about 8 – 10 hours for the selected additive ratio of 0.4% M-ADS 1 and 0.6% M-ADW 1. Good green strength of 24 MPa is achieved after 24 hours (table 2). VIB 5M containing only phosphate additives STPP and SHMP show comparable EXO Max and green strength results. However, to avoid flow decay with STPP and to achieve extended working times with phosphates in general, the addition of citric acid is often required. As a consequence the strength development is delayed. Citric acid additions in the range of 0.03 – 0.07% only slightly increase the working time, but significantly retard the cement hydration and strength development. E.g. the addition of 0.03% citric acid retards the EXO Max peak of VIB 5M-SHMP to 30h and 0.07% to 66h. Such long de-moulding times are often not acceptable for both on-site installations and pre-cast shape production.

Figure 7 shows cold crushing strength at 20°C after 24 hours curing and EXO Max of all additive packages tested in VIB 3M. It is clear that a late EXO Max results in low curing strength after 24h. Castables with an EXO Max above 24 hours have insufficient green strength for de-moulding, handling and transport. Mechanical damage of the cast piece or lining is very likely and may often be discovered at a later stage during drying or firing of the material. M-ADS/W dispersed castables achieve high green strengths due to a reliable early exothermic reaction for all adjusted ratios.

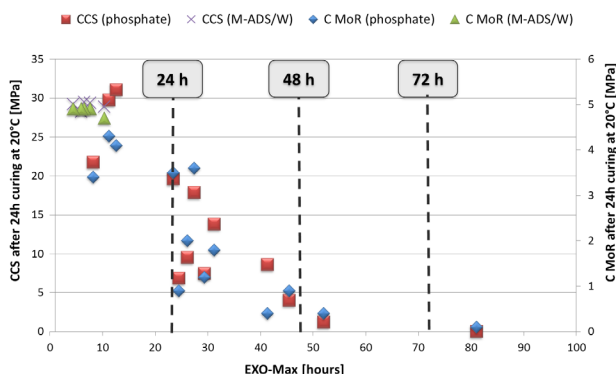


Fig. 7: Curing strength after 24h vs. EXO Max tested in VIB 3M.

The impact of citric acid on the cement hydration was further investigated with heat flow calorimetry under tightly controlled conditions using a paste based on tabular alumina -45MY Li and containing 20% cement, 10% reactive alumina RG 4000, 3% silica fume, and 0.1% polyphosphate. Citric acid was added in the range of 0 – 0.08%. The heat flow curves show two distinct peaks, a smaller sharp peak (I) within the first hours and a later broader peak (II) which comes from the main cement reaction (figure 8).

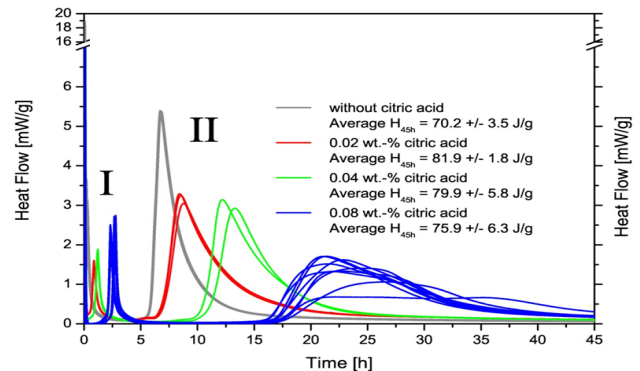


Fig. 8: Heat flow of test paste with 3% silica fume, 0.1% polyphosphate and different additions of citric acid.

The first peak is caused by a reaction of phosphate in combination with cement, but it is not related to hydration of the cement and produces only a small amount of heat and therefore strength in technical castables. It is this reaction which leads to a “stiffening” [1] and the end of workability of refractory castables dispersed with phosphate additives. This stiffening usually occurs rather quickly within the first hour(s) after casting and is often considered as the start of setting and the cement hydration. However, it is obvious that the cement hydration only occurs hours later. As shown in figure 8, this first reaction can be retarded by citric acid with a roughly linear relationship between citric acid amount and retardation achieved. This makes the use of citric acid as a retarder so popular in the industry. However, the citric acid also has a retarding effect on the main reaction (II) but here the relationship is far from being linear. Small increases of citric acid result in strong retardation of the main reaction and at 0.08% citric acid the intensity of the reaction also becomes weaker. This is shown by a broader and flat peak in figure 8. This confirms the observations made with the test castables at increasing amounts of citric acid, where EXO Max becomes very long and sometimes not easy to detect because of the flat broad peaks. This indicates a hampered sub-optimal cement hydration reaction.

In order to check the strength development of phosphate dispersed castables in comparison to M-ADS/W castables, strength testing of castables with 97% grade silica fume and selected additive systems (table 2) was performed parallel to ultrasonic and exothermic reaction measurements during curing (figure 9 and 10). For the dispersing alumina castable the increase in ultrasound velocity correlates well with the strength development (figure 9). The phosphate/citric acid castables show a stepped increase of US velocity where a first increase to 3-4000 m/s cannot be related to a measurable cold crushing strength which only appears after further increase of US velocity which takes place after 20 to 24 hours. The CCS level of these castables after 24 hours curing is significantly lower when compared to the dispersing alumina castable, and only after 48 hours curing are they on the same level.

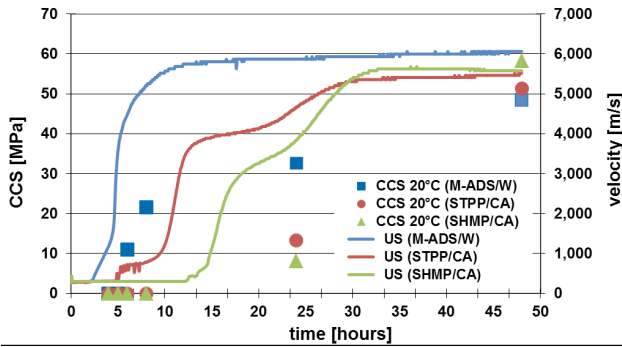


Fig. 9: VIB 5M - Ultrasonic velocity and CCS at 20°C/24h.

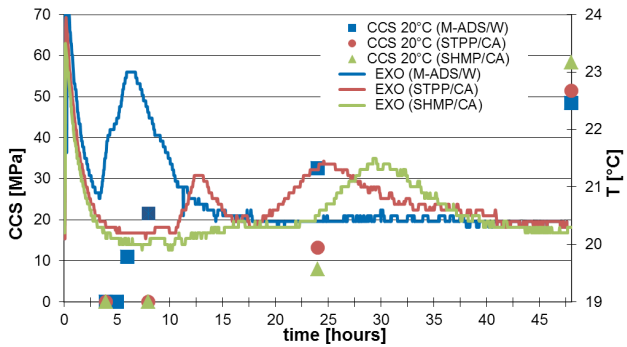


Fig. 10: VIB 5M - Exothermal reaction and CCS at 20°C/24h.

It becomes obvious, that the stiffening reaction with phosphates is sufficient to increase the US velocity significantly but still no real strength development is taking place. Therefore US measurements of phosphate castables must be evaluated and considered with care and focus should be made on the subsequent increase of US velocity. The EXO measurement provides reliable data for the strength development. Figure 10 shows how well the EXO peak correlates with the strength development. For dispersing alumina castables the US and EXO curves correlate well and the increase in the curves comes from the main cement reactions from which the strength develops.

#### Aging resistance of dry castable mixes

Short term aging tests up to 14 days were performed for the test castables with dispersing alumina and test mixes containing STPP or SHMP with and without 0.03% and 0.05% citric acid addition. The setting was measured with the EXO method for the fresh dry mix and for dry mixes aged up to 14 days at 20°C and 65% relative humidity. Figure 11 compares the EXO Max results of the test mixes. VIB 5M dispersed with M-ADS/W shows an early EXO Max for the fresh mix which remained stable over 14 days open storage. The same applies for the 0.1% STPP containing mix without citric acid. Castable with 0.05% SHMP started at a longer EXO Max which increased slightly over storage time. The castables containing STPP or SHMP plus citric acid as retarder already show a long EXO Max at the starting point. After 14 days storage the working time has changed significantly, e.g. from initially 36 hours to 64 hours for the mix with 0.05% SHMP and 0.05% citric acid.

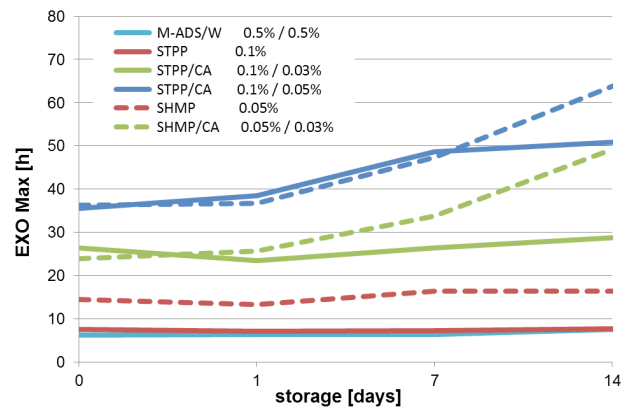


Fig. 11: VIB 5M – Short term aging of dry mix up to 14 days

The change in castable behaviour over a short storage period for the phosphate/citric acid systems is very critical and increases the risk of failure during installation. Quality control (QC) testing is not able to monitor the changes happening during storage because the testing is normally performed during or shortly after manufacturing.

#### Additives re-adjustment

Re-adjustment of a ready pre-mixed castable can become necessary due to irregular material consumption, longer storage times and changed ambient conditions on-site, which impact the setting behaviour of a castable. When traditional additive systems are used, where generally small amounts are added, re-adjustments can become very critical. Correct dosing of small amounts of citric acid (e.g. 0.02%) for retardation and even much smaller amounts of an accelerator (e.g. 0.002% of Lithium carbonate) is extremely difficult to carry out on site. Over-dosing can have drastic effects such as never-setting of the castable or conversely flash-setting in the mixer. Dispersing alumina castables provide the opportunity for easily manageable re-adjustment, both for retarded and accelerated setting. Figure 12 shows the option for later retardation of a low cement castable with 5% silica fume, initially adjusted with 0.1% M-ADS 1 and 0.9% M-ADW 1. A further addition of 0.4% M-ADS 1 extends the working time by about 2 hours and the de-moulding time by about 2.5 hours. For the investigation of later acceleration a castable with long setting was used. This contained 0.9% M-ADS 3 and 0.1% M-ADW 1. The addition of the normally accelerating additive M-ADW 1 in the range of 0.4% did not change the setting pattern of the mix. This may be attributed to a retarding effect by additional dispersing agent, which compensates the acceleration of additionally dosed M-ADW 1. However, accelerated setting can be achieved by the addition of Alphabond 300 [5] up to 0.5% as shown in figure 13.

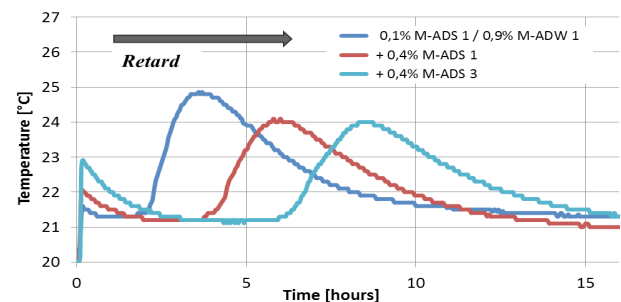


Fig. 12: VIB 5M-DA re-adjustments for retardation.

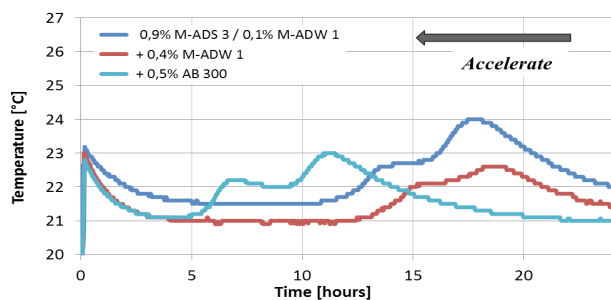


Fig. 13: VIB 5M-DA re-adjustments for acceleration.

## CONCLUSION

Traditional additive systems for silica fume containing low cement castables such as different phosphates in combination with citric acid have been compared to the modern polymer based dispersing alumina system M-ADS/W. In addition to the flow behaviour at different dosing levels the cement hydration and strength development has also been investigated with regard to the practical requirements for monolithic linings and pre-cast shape manufacturing. Also, other important practical aspects such as the aging resistance of dry mixed castables during storage and options for the re-adjustment of working and setting time on-site were discussed. Phosphate based additive systems are low cost solutions when compared to dispersing aluminas, but they have several disadvantages with regard to control of working time and strength development, sensitivity to slight over-dosages of citric

acid, and lower storage stability especially when containing citric acid.

Overall, dispersing aluminas provide a much more robust system which strongly contributes to reliable castable performance and avoids installation failures and the frustrating consequences of such failures which may lead to complaints. The higher price of this modern solution is therefore money well spent when the cost/performance ratio is taken into account, especially for more demanding applications where reliable performance is essential.

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