

THE VALUE OF ADDITIVES IN REFRACTORY CASTABLES – CASTABLES WITHOUT SILICA FUME

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INTRODUCTION

The matrix of low cement castables contains fine and ultra-fine particles such as calcium aluminate cement, reactive aluminas and other fines of synthetic or natural origin. It is essential that all the matrix components are distributed homogeneously during mixing with water to take full advantage of the optimised particle size distribution, thereby achieving the lowest possible water demand and the desired rheological behaviour. Efficient additives are of high importance to achieve this target. Furthermore, apart from dispersion, additives have to serve various functions regarding castable setting time and workability under different placement and climatic conditions. Key requirements for additives in modern low cement castable design are:

- Optimum castable dispersion/flow properties at lowest possible water demand
- Adjustment of setting/working time under different temperature and placement conditions
- Reliable, secure and homogeneous dosing and distribution of the additives
- Robust, reliable and reproducible strength development within an acceptable time
- Achieving an overall high castable performance with best mechanical strength and hot properties and gaining optimum benefit from the high value matrix fines used
- Aging resistance of dry mixed castables
- Optional re-adjustment of setting/working time under changing conditions during on-site installation

This paper discusses the differences between widely used traditional organic and inorganic additives and advanced additives such as Dispersing Alumina which contain highly efficient polymers.

DISPERSING ALUMINAS

Dispersing aluminas were first introduced by Kriechbaum et al. [1], and now comprising a separately optimised product range for silica fume free and silica containing castables. They are designed as a co-formulation of modern organic additives with reactive alumina and other inorganic materials. Table1 shows the product range for silica fume free castables, also including castables with max. 1% silica fume, where silica fume does not directly serve as the matrix fine filler but is used to control the expansion of spinel forming castables.

Tab. 1: Typical product data - dispersing aluminas for silica fume free castable

Product	ADS 1	ADS 3	ADW 1
Effect	Retarding	Strong retarding	Accelerating
Chemical Composition	[%]		
Al ₂ O ₃	80	76	80
Na ₂ O	0.10	0.10	0.10
B ₂ O ₃	0.80	2.80	0.03
CaO	1.80	1.80	1.80

Dispersing aluminas in general serve two main functions, in addition to highly efficient matrix fines dispersion, they enable adjustable setting control depending upon specific placement requirements and climatic condition.

Fig.1 shows an illustrative example of the set control (working time) by using various proportions of the accelerating ADW 1 and retarding ADS 3.

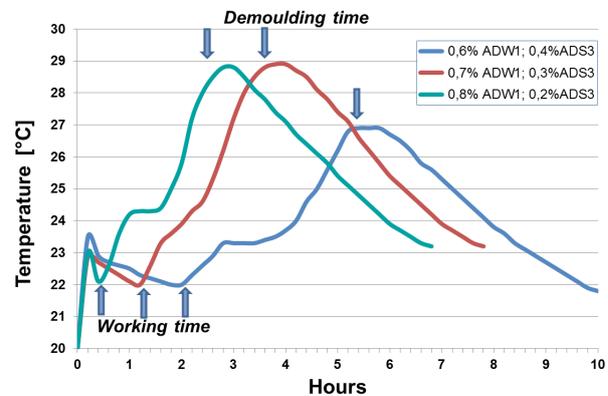


Fig. 1: Castable working time and demoulding time adjustability

The recommended total amount is about 1% for low cement castables. The strength development (EXO max. equals demoulding strength) has an almost linear relationship with the working time.

TEST CASTABLE AND ADDITIVE SELECTION

A low cement vibration castable with various additives was selected for the test series.

Apart from dispersing alumina, a commonly used polyacrylate and sodium-tripolyphosphate were chosen. Detailed information on these widely used additives is available from [2].

Additive and water addition were adjusted to comparable vibration flow data at lowest possible water addition, as follows:

- “VIB 4 DA” with 4.2% mixing water and 1% dispersing alumina (0.4 % ADS 3 and 0.6% ADW 1)
- “VIB 4 DA5” included for comparison purpose only, with 5% mixing water requirement - the same as the other two additive test mixes
- “VIB 4 PA” with 5.0% mixing water and 0.1% poly-acrylate
- “VIB 4 STPP” with 5.0% mixing water and 0.08% sodium-tripolyphosphate.

During the first experiments, the mixes using polyacrylate and STPP showed significant flow decay with no acceptable vibration flow at 60 minutes (F60) in particular, hence an addition of citric acid as a commonly used set retarder became necessary.

Fig.2 and Fig.3 show the adjustment for optimum flow and acceptable flow decay, in both cases achieved with 0.05% citric acid addition.

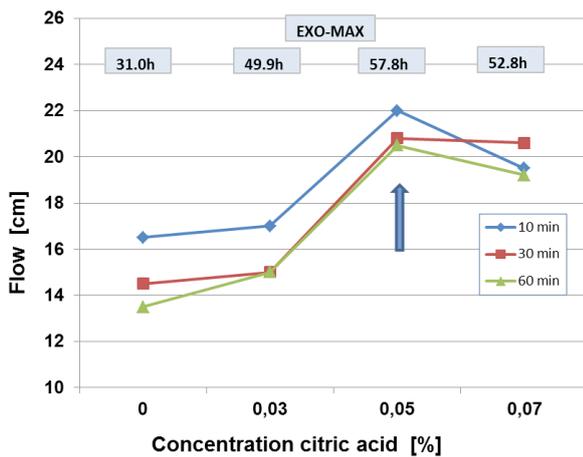


Fig. 2: VIB 4 with 0.1% polycrylate and citric acid addition

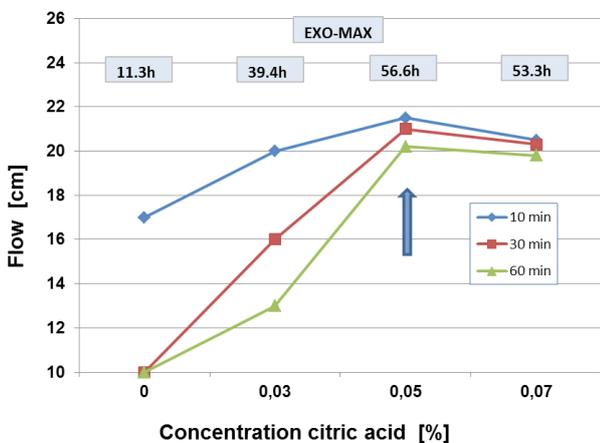


Fig. 3: VIB 4 with 0.08% STPP and citric acid addition

As a consequence, the EXO max. which correlates to sufficient strength for demoulding, went up to above 50 hours.

The finally selected test recipes and all measured data are shown in Tab.2.

Tab. 2: Test mix compositions and test results

Mix		VIB 4 DA	VIB 4 DA5	VIB 4 PA	VIB 4 STPP	
Components		[%]				
T60/T64	up to 6 mm	82	82	82	82	
Alumina	CL 370	13	13	13	13	
Cement	CA-14 M	5	5	5	5	
Additives	ADS 3	0.4	0.4	-	-	
	ADW 1	0.6	0.6	-	-	
	Polyacrylate	-	-	0.1	-	
	STPP	-	-	-	0.08	
	Citric Acid	-	-	0.05	0.05	
H ₂ O		4.2	5	5	5	
VIB-Flow	10 min	22.0	24.3	22.0	21.5	
	30 min	22.0	24.0	20.8	21.0	
	60 min	21.8	24.2	20.5	20.2	
EXO	Start 1	102' / 21.4 °C	172' / 22.0 °C	n. d.	76' / 22.0 °C	
	Start 2	4.4 h / 21.6 °C	5.4 h / 22.6 °C	52.3 h / 20.6 °C	46.0 h / 19.8 °C	
	Max	6.4 h / 25.9 °C	7.4 h / 25.6 °C	57.8 h / 21.9 °C	56.6 h / 21.7 °C	
Density	1000°C	[g/cm ³]	3.13	3.08	3.14	3.12
Open porosity	1000°C	[%]	15	17	15	16
CCS	20°C / 24 h	[MPa]	24	21	7	6
	110°C / 24 h	[MPa]	86	82	79	52
C MoR	20°C / 24 h	[MPa]	4	4	1	1
	110°C / 24 h	[MPa]	17	15	11	10
HMoR 1500°C	(pre-fired 1000°C/5h)	[MPa]	19	17	13	6
	(pre-fired 1500°C/5h)	[MPa]	23	18	16	4

Individual results and additional observations are discussed in the following parts of this paper.

CASTABLE SETTING AND STRENGTH DEVELOPMENT

Castable setting behaviour was determined by the exothermal method (EXO) and partially by measuring the ultrasonic velocity (US). Details of both methods and terminology were described by Gierisch et al.[3].

VIB 4 DA and the intentionally overwatered VIB 4 DA5 show practical working times (EXO start 1) ranging from 2-3 hours, and a relatively short strength development to demoulding time (EXO max.).

However, both VIB 4 PA and VIB 4 STPP clearly show a delayed strength development with EXO max. of the order of more than 2 days (56-58h), which is attributed to the required addition of citric acid (see Fig. 2&3 and Tab.2).

Cold crushing strength (CCS) and cold modulus of rupture (CMoR) were measured after 24h curing at 20°C and after 24h drying at 110°C.

Fig.4 shows CCS and CMoR for the 24h curing, commonly known as green strength.

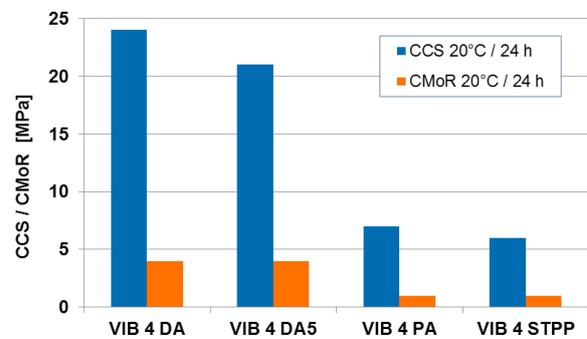


Fig. 4: CCS and CMoR at 20°C / 24 h

The mixes using dispersing alumina as an additive generally show a high level of green strength within 24h, VIB DA5 shows slightly less with 0.8% more mixing water than is required.

Due to the retarded strength development both VIB 4 PA and VIB 4 STPP have very low green strength, CMoR's in particular are

only 1 MPa. Such low strength makes transport of larger pre-cast shapes impossible even after 24h curing. The results for the commonly called dried strength (24h at 110°C) are shown in Fig.5.

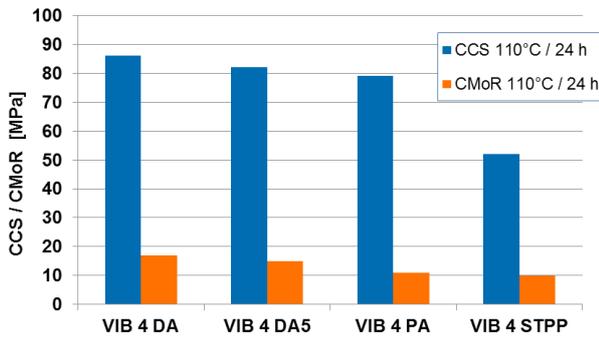


Fig. 5: CCS and CMoR at 110°C / 24 h

The expression “dried strength” however is somewhat misleading as a castable is never completely “dry” at 110°C. Firstly there is chemical combined water within the hydrated calcium aluminate cement particles. Secondly there is still superficial water present due to the steam pressure in the small pores (hydrothermal condition) which is only released at temperatures beyond 200°C.

Also here, the mixes using dispersing alumina show the highest CCS and CMoR. VIB 4 PA with its additive being similarly of organic nature, reaches practically the same strength level as the comparable VIB DA 5 with 5.0% mixing water by additional cement hydration during the drying at 110°C/24h. The retarded strength development caused by the citric acid addition in VIB 4 PA and VIB 4 STPP has now been overcome. However VIB 4 STPP remains at a general lower “dried strength” level. This could only be attributed to structural effects, as castable density and porosity (see Table 2) are comparable to the other mixes.

Further testing has shown that mixes using phosphates/citric acid dispersion can give an impression of early hardening, however it is only a physical stiffening and does not correlate with true strength development. A precipitation of hydroxylapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is suggested as a possible explanation for this stiffening effect.

The ultrasonic velocity method (US) confirms this, as the first velocity rise is usually interpreted as hardening and the start of true strength development.

In practice this could mean that this stiffening effect with, however, insufficient strength, could lead to a decision to de-mould at a time when the castable is still “moveable”, resulting in severe consequences with additional downtime and subsequent additional cost.

Fig.6 compares mixes dispersed with dispersing alumina (ADS/W) and phosphate/citric acid (Phos./Citr.). showing ultrasonic velocity and the corresponding CCS at 20°C.

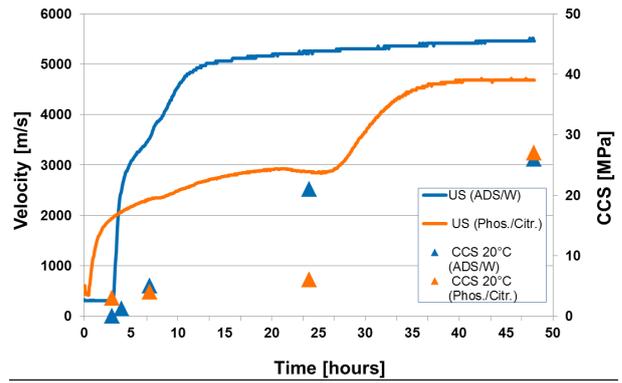


Fig. 6: VIB 4: Ultrasonic velocity and CCS at 20°C / 24 h

The mix with dispersing alumina shows a clear and single velocity rise with gradually increasing strength development. The mix with phosphate/citric acid dispersion shows a very early velocity rise, usually indicating end of working time and start of strength development, however CCS starts to rise significantly only after the 2nd slope after about 25 hours. In consequence, the ultrasonic method can be misleading for phosphate/citric acid dispersed mixes and should be supported by EXO measurements.

Fig. 7 shows the same test series carried out via EXO method.

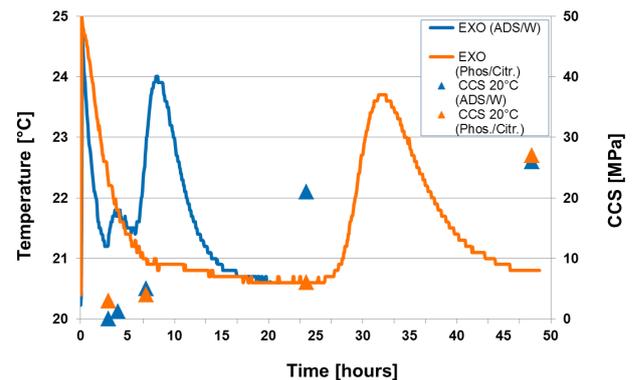


Fig. 7: VIB 4 Exothermal reaction and CCS at 20°C / 24 h

The exothermal heat development for the ADS/W mix correlates with the results from the ultrasonic method. For the mix with phosphate/citric acid dispersion it becomes very clear that the true strength development coincides with the first significant temperature rise, which begins only after about 25 hours.

HOT PROPERTIES

For the 4 test mixes, hot modulus of rupture (HMoR) was performed at 1500°C. Test bars were pre-fired at 1000°C and 1500°C.

The results are shown in Fig.8.

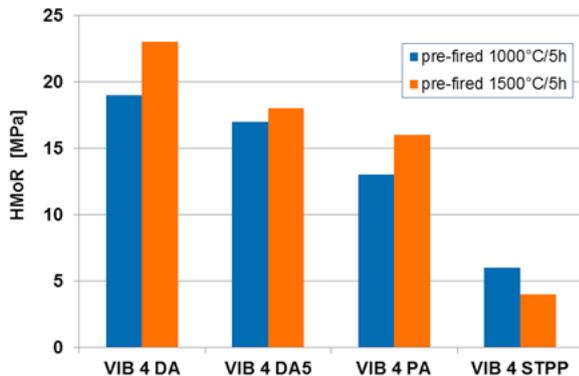


Fig. 8: Hot modulus of rupture (HMoR) at 1500°C

The results practically show the same trend observed for the 110°C CCS and CMoR measurements.

VIB 4 DA showed the highest HMoR. VIB 4 DA5 was slightly lower because of decreased density and increased porosity due to the additional 0.8% mixing water.

VIB 4 PA does not reach the same HMoR as the mix with dispersing alumina using the same 5.0% mixing water. This is attributed to the proportion of matrix strengthening reactive alumina in dispersing aluminas, which further adds to increased HMoR.

The mix with phosphate/citric acid dispersion, VIB 4 STPP, shows considerably lower HMoR, similar to the 110°C/24h strength. It is assumed that besides structural effects, also a chemical effect of the phosphate contributes to the lower hot strength by forming trace amounts of low melting phase. This would explain that such a mix only achieves about 30% HMoR of a comparable mix with dispersing alumina. This assumption is further supported by a drop in HMoR at 1500°C pre-firing versus 1000°C pre-firing, while all other mixes showed increasing HMoR indicating proper sintering. Most remarkable is that such a small dosage of 0.08% STPP has this effect on hot properties.

ADDITIVES DOSING

Additives usually represent the lowest proportion by weight of a castable formulation. At the same time they must be totally reliable when considering castable processing and product parameters. Consequently, the correct dosage of these small amounts is absolutely essential to ensure mixing, placement and setting properties as intended when a given castable recipe is developed. Small deviations, which can result from inaccurate weighing or segregation during bagging of dry mixed castables are prone to cause significant processing and product property changes.

For low cement castables, the recommended addition of dispersing alumina is 1.0%. This equates to 10kg of material to be dispersed in a 1000kg dry mix. This is an amount which ensures correct dosage, homogeneous dispersion during dry mixing and minimized segregation during conveyance of a dry mix.

Other additives, e.g. the selection used for the test series, require additions of only 0.1% or even lower. As seen for example in Fig.5 or Fig.6, small deviations of citric acid proportions in the magnitude of 0.02% have a significant impact on castable flow properties and strength development. This low proportion of 0.02% equates to 200g of material in a 1000kg batch size. If such

a batch size is delivered in 40x25kg bags, a bag-to-bag variation of only 5g of citric acid would show very significant castable flow and setting time variations. Therefore, it becomes clear that a precise and homogeneous distribution of such small additive percentages is difficult to achieve in practice.

AGING RESISTANCE OF DRY CASTABLE MIXES

Storage stability of dry castable mixes is becoming increasingly important. Globally growing export business with long lead times, or project business with irregular material consumption require the castable properties to remain unchanged between manufacturing date (incl. QC testing) and its final installation within the required time frame. Experiences have shown that dry mixed castables can change over time with respect to flow and setting properties. This mainly results from an interaction between the binder, e.g. calcium aluminate cement, and the additives.

The aging behaviour of properly warehouse-stored dry mixed castables using different additives was comprehensively investigated by Gierisch et al.[3]. The paper includes comparisons between dispersing aluminas ADS/W and polyacrylate/citric acid additive in low cement castables under proper warehousing conditions. Bagged dry LCC mixes with dispersing aluminas showed a storage stability and consistency in bi-monthly measurements taken over the reporting period of 9 months. Subsequent measurements confirmed storage stability over 12 months. Therefore castable flow and setting time remained practically unchanged for the period of one year.

The polyacrylate/citric acid additive system showed a gradual drop in flow properties starting at about 7 months storage, and did not flow with the specified mixing water addition after 9 months. Regarding commonly used additives as e.g. citric acid, Krebs[4] reported about significantly retarded working/setting times from an initially adjusted 45min. and increasing to 220min. over a period of only 8 days!

The often practiced counter-steering procedure with e.g. Lithium-Carbonate for re-acceleration is critical, as very small amounts, e.g. 0.002% (=20g per 1000kg castable!) are recommended, thus bearing the risk of overdosing which can quickly reverse the effect from retarded setting into flash setting.

ADDITIVES RE-ADJUSTMENT

There are several reasons why re-adjustments of initially specified and controlled castable settings can be needed in practice:

- Retardation at high ambient temperatures or large volume installations
- Acceleration at low ambient temperatures
- Very tight on-site setting time adjustments needed in precast shape manufacturing, e.g. for timely cone removal in case of well block manufacturing.

As indicated previously, when conventional additives are used, where generally small amounts are required and prolonged strength development occurs, re-adjustments can become very critical.

Castables using dispersing alumina allow convenient re-adjustments, both for retarded and accelerated setting.

Fig.9 shows retarding and acceleration options for a VIB 4 type vibration LCC, initially adjusted with 0.6% ADS 3 and 0.4% ADW1.

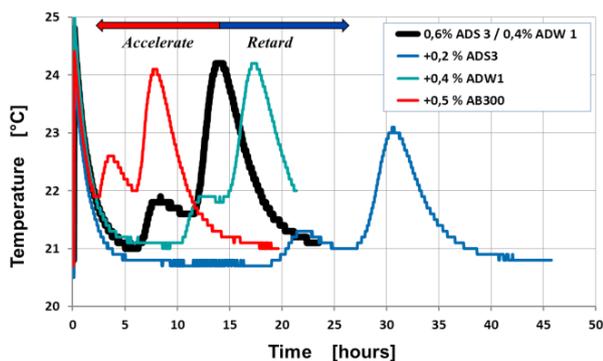


Fig. 9: VIB 4 re-adjustments for retardation and acceleration

A further addition of 0.2% ADS 3 retards the setting, which could be required if the given formulation needs to be mixed and installed under high temperature conditions, e.g. castable shipped to a region with hot climate. The addition level of ADS 3 can be tailored to individual needs.

Interestingly, a 0.4% addition of normally accelerating ADW 1 also led to a slightly retarded setting. This can be attributed to the observed retarding effect of additional dosing with modern organic polymers, as reported by Seyerl[5]. Thus, the proportional retardation with increasing organic polymer amounts dominates the accelerating component in ADW 1.

However, overall acceleration of a given formulation with dispersing alumina can be achieved by the addition of Alphasbond 300. The example shows that an addition of only 0.5% is sufficient to achieve an accelerated setting.

CONCLUSION

The investigations of three different additive concepts have shown their individual properties and effects on a selected low cement vibration test-castable. Both, the commonly used polyacrylate and phosphate additives, do not entirely satisfactorily de-

liver the performance under the various conditions which modern castable design require.

Related problems addressing overall castable performance reliability and robustness, settings, storage, aging and disturbed or delayed installations would now represent a significant cost implication.

Dispersing aluminas provide unique features as highly efficient dispersants for lowest possible mixing water requirement and freely adjustable setting times depending upon climatic and placement conditions. Further benefits are secure dosing, optimised castable installation and excellent physical properties. Long castable dry mix shelf-life and optional re-adjustments contribute to simplified material management and installation flexibility. This makes dispersing aluminas a true “convenience product”, therefore providing a significant value addition to modern castable design.

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Data citation:

- Proceeding title, see above
- Proceeding no., see above
- Authors' names, see above
- Source: USB-Stick UNITECR2015 – 14th Biennial Worldwide Congress
- ISBN 978-3-9815813-1-7
- urn:nbn:de:101:1-201506294612