Review of Dispersing Alumina and the Matrix Advantage System 25 Years after Launch

R. Kockegey-Lorenz, A. Buhr, D. Schmidtmeier, S. Klaus

Since the launch of the Dispersing Alumina and the Matrix Advantage System, the concept has contributed to a quantum leap in castable technology with installation behaviour and technical properties on new levels. Practical industrial experience has proven the value of the system and it has become a standard in many applications. This paper reviews the essential components and their application for different requirements and discusses new developments. User friendliness has always been the driving force in the developments and is very important to ensure maximum value in use, especially for monolithic installations.

1 Introduction and historical development of Dispersing Aluminas

In 1996 Kriechbaum et al. [1] first described a group of newly developed fine materials, the Matrix Advantage System (MAS), which consisted of Reactive Alumina, Reactive Alumina/Spinel, Calcium Aluminate Cement and Dispersing Aluminas. The two Dispersing Aluminas, ADS 1 and ADW 1, have bi-modal particle size distributions and contain organic and inorganic ingredients to improve dispersion and allow setting characteristics to be controlled. ADS 1 has been specifically designed to improve dispersion and enable controlled retarding properties in a cement bonded system. ADW 1 also improves dispersion, but offers the option to accelerate the setting of a cement bonded castable. These two Dispersing Aluminas were optimised to perform best in silica fume free castables or those with max 1 % silica fume, where silica fume does not directly serve as a matrix fine filler but is used to control the expansion of spinel forming castables.

Rapidly increasing interest for these two Dispersing Aluminas, along with growing export into warmer regions and the consequent need for sufficiently long working times in those regions, led to the development of the stronger retarding ADS 3 which was subsequently introduced in 1997.

Tab. 1 Typical product data – Dispersing Aluminas for silica fume free castables

Product		**ADS 1**	**ADS 3**	**ADW 1**
Effect		Retarding	Strong retarding	Accelerating
Typical chemical composition [%]	Al_2O_3	80	76	80
	Na_2O	0,10	0,10	0,10
	B_2O_3	0,80	2,80	0,03
	CaO	1,80	1,80	1,80
L.o.I. at 1050 °C		18,0	20,0	18,0
Particle size D50 Cilas [µm]		2,6	2,6	2,6
Particle size D90 Cilas [µm]		9,0	9,0	9,0

The three grades of Dispersing Aluminas are shown in Tab. 1. These combine highly efficient matrix fines dispersion with adjustable setting control depending upon specific placement requirements and climatic condition.

Following the success of this new and unique performing product line, market demand led to the development of Dispersing Aluminas specifically targeted at silica fume containing low cement castables. Following the same concept for dispersing alumina, M-ADS 1 and M-ADW 1 were developed and first introduced in 2000 by Van Garsel et al. [2].

With the introduction of the new temperature independent Calcium Aluminate Cement CA-470 TI in 2007 by Buhr et al. [3], a stronger retarding grade was required for silica containing castables and therefore M-ADS 3 was developed. The product line

Rainer Kockegey-Lorenz, Andreas Buhr,
Dagmar Schmidtmeier, Sebastian Klaus
Almatis GmbH
Frankfurt/Ludwigshafen, Germany

Jerry Dutton
Stourbridge, Great Britain

Corresponding author: *R.Kockegey-Lorenz*
E-mail: Rainer.Kockegey-Lorenz@almatis.com

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Tab. 2 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
Typical chemical composition [%]	Al_2O_3	91	95	96
	Na_2O	1,40	1,40	0,10
	B_2O_3	1,30	2,50	0,55
	CaO	0,02	0,02	0,02
L.o.I. at 1050 °C		7	8	2,7
Particle Size D_{50} Cilas [µm]		2,6	2,6	2,6
Particle Size D_{90} Cilas [µm]		9	9	9

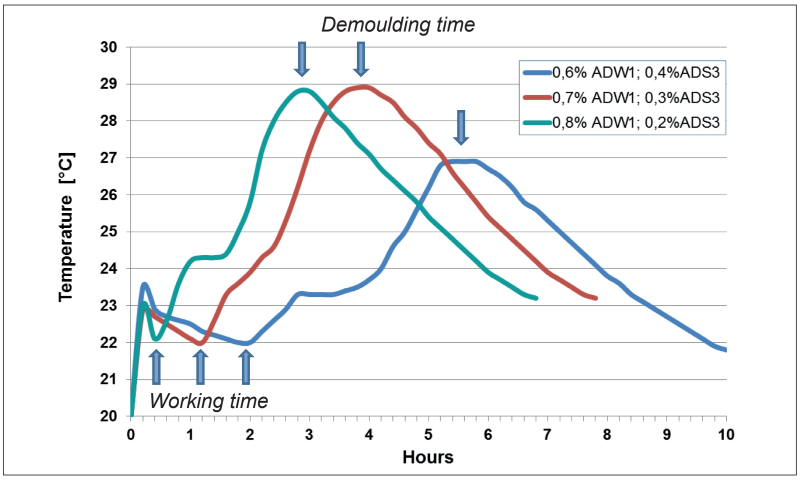

Fig. 1 Castable working time and demoulding time adjustability

Tab. 3 Test mix composition and test results

Mix		VIB 4 DA	VIB 4 PA
Tabular T60/64 [%]	up to 6 mm	82	82
Alumina [%]	CL 370	13	13
Cement [%]	CA-14 M	5	5
Additives [%]	ADS 3	0,4	–
	ADW 1	0,6	–
	Polyacrylate	–	0,1
	Citric acid	–	0,05
H_2O [%]		4,2	5
VIB-Flow [cm]	10 min	22,0	22,0
	30 min	22,0	20,8
	60 min	21,8	20,5
EXO	Start 1	102'/21,4 °C	n.d.
	Start 2	4,4 h/21,6 °C	52,3 h/20,6 °C
	max	6,4 h/25,9 °C	57,6 h/21,9 °C
CCS [MPa]	20 °C/24 h	24	7
	110 °C/24 h	86	79
C-MoR [MPa]	20 °C/24 h	4	1
	110 °C/24 h	17	11
HMoR 1500 °C [MPa]	pre-fired 1000 °C/5 h	19	13
	pre-fired 1500 °C/5 h	23	16

of Dispersing Aluminas for silica fume containing castables is shown in Tab. 2.

Therefore two individually optimised systems for both silica-free and silica containing LC (Low Cement) castables are now available.

2 Value and features of Dispersing Aluminas

The value of additives was comprehensively discussed by Kockegey-Lorenz et al. [4] for silica fume free LC castables and by Schnabel et al. [5] for silica fume containing LC castables. This included a comparison of the dispersing alumina concept with traditionally used organic and inorganic additive systems. It highlighted the multiple advantages of Dispersing Aluminas.

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.

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 conditions. Fig. 1 illustrates the set control (working time) by using various proportions of the accelerating ADW 1 and retarding ADS 3. This paper discusses a selection of properties and features from [4] and [5] with examples for a silica-free vibration castable.

Tab. 3 shows two LC vibration castable test mix formulations comparing dispersion, set control and physical properties of VIB 4 DA with 1 % dispersing alumina (0,4 % ADS 3 and 0,6 % ADW 1) and VIB 4 PA with 0,1 % polyacrylate and 0,05 % citric acid.

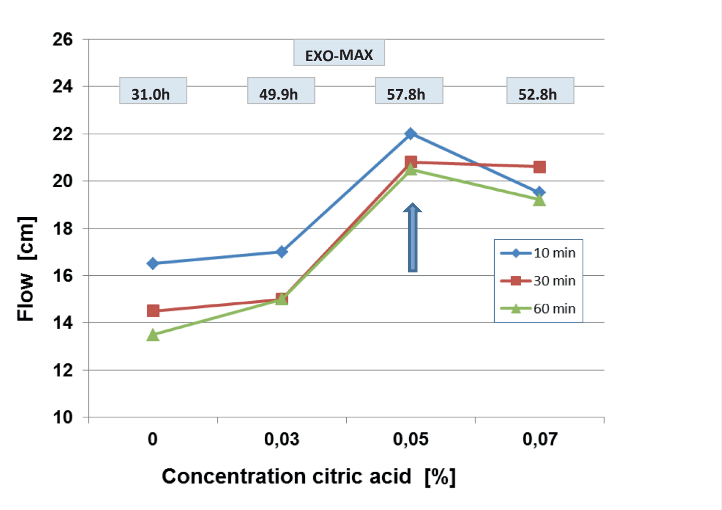

Fig. 2 VIB 4 PA with 0,1 % polyacrylate and citric acid addition

2.1 Flow properties – dispersion

The mixing water of the two mixes is adjusted to give the same initial flow diameter of 22,0 cm after 10 min (F10).

For this same flow diameter, the mix with dispersing alumina requires only 4,2 % mixing water, whereas the mix with polyacrylate/citric acid requires 5,0 %. The difference in water requirement has a significant influence on strength results. For VIB 4 PA, an addition of citric acid is necessary to achieve the targeted flow diameter.

Fig. 2 shows flow results with incremental additions of citric acid to the 0,1 % polyacrylate. A remarkable and undesired side-effect of the citric acid addition is the extremely prolonged strength development/demoulding time in addition to the general retarding effect of a polyacrylate dispersion, finally resulting in a set of >2 days.

2.2 Mechanical strength properties

As a result of the lower mixing water required for VIB DA, mechanical strength (CCS and CMoR as green strength, 20 °C/24 h curing) and dried strength (110 °C/24 h drying) is significantly higher than that of VIB PA. Likewise the Hot Modulus of Rupture (HMoR) measured at 1500 °C is higher for VIB 4 DA, regardless of pre-firing at 1000 °C/5 h or 1500 °C/5 h.

The low green strength (CCS 20 °C/24 h) of VIB 4 PA can be explained by retarded strength development seen by the prolonged EXO max >50 h with the corresponding effect on low cured strength after 24 h.

In this context, it is worthwhile mentioning that the often practiced counter-steering procedure using e.g. lithium carbonate for re-acceleration is critical, as very small amounts, e.g. 0,002 % (= 20 g per 1000 kg castable!) are recommended, therefore introducing the risk of overdosing which can quickly reverse the effect from retarded setting into too fast and even flash setting.

2.3 Dosing matters

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 which were intended when a given castable recipe was 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 10 kg of material to be dispersed in a 1000 kg dry mix. This is an amount which ensures correct dosage, homogeneous dispersion during dry mixing and minimised 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. 2, very small increments 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 200 g of material in a 1000 kg batch size. If such a batch size is delivered in 40 kg × 25 kg bags, a bag-to-bag variation of only 5 g 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.

2.4 Dry castable mix – aging

Storage stability of dry castable mixes is becoming increasingly important. Globally growing export business with long lead

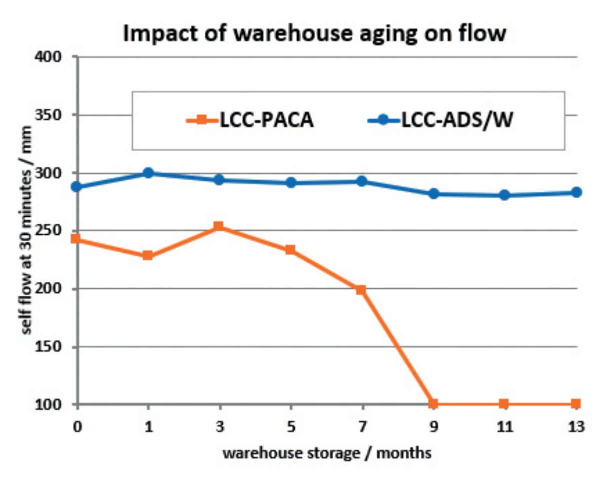

Fig. 3 Dry mix castable aging, impact on flow properties

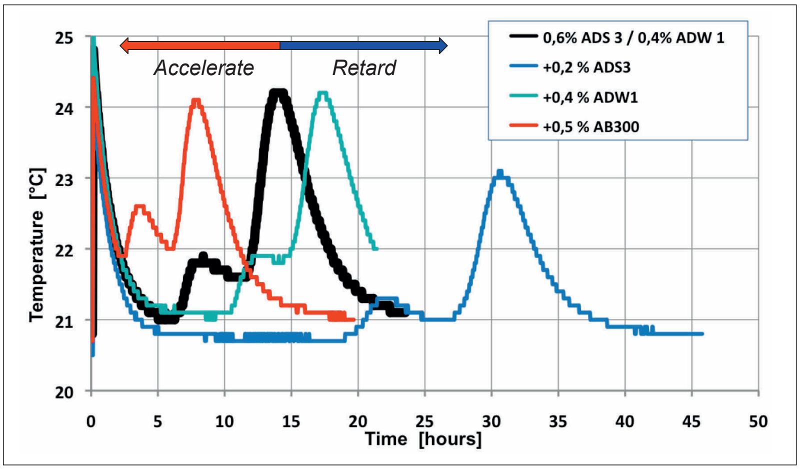

Fig. 4 VIB 4 DA re-adjustments for retardation and acceleration

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. [6]. The paper includes comparisons between Dispersing Aluminas ADS/W and polyacrylate/citric acid additives 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 at least one year.

The polyacrylate/citric acid additive system showed a gradual drop in flow properties starting after about 7 months storage, and did not flow with the specified mixing water addition after 9 months as shown in Fig. 3.

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 during 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. 4 shows retarding and acceleration options for the VIB 4 DA vibration LCC, initially adjusted with 0,6 % ADS 3 and 0,4 % ADW1. 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 a 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 leads to a slightly retarded setting. This can be attributed to the observed retarding effect of additional dosing with modern organic polymers. Therefore 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 Alphabond 300. The example shows that an addition of only 0,5 % is sufficient to achieve an accelerated setting. Further details on that are discussed in detail by Kuiper et al. [7].

2.5 New developments

A widely used retarder for CA cement bonded castables other than citric acid, with its obvious drawbacks with regard to prolonged strength development etc., is boric acid. Since 2010, boric acid has been classified as a SVHC. The retarding grades of dispersing alumina use boric acid because of its advantageous set-retardation behaviour within reasonable time frames. Therefore boron is listed in the respective SDS's (Safety Data Sheets).

In the event of the EU-commission imposing further regulatory measures in the future, Almatis has proactively developed a boric acid free equivalent to ADS 3, called ADS 3 FREE.

Remark: The small amount of (typically 0,03 % = 300 ppm) B_2O_3 has its source in the low soda reactive alumina and is at the same level as the boron-free ADW 1.

Tab. 4 Typical product data – new boron-free Dispersing Alumina ADS 3 FREE

ADS 3 FREE		
Effect		Strong retarding
Typical chemical composition [%]	Al_2O_3	73
	Na_2O	0,10
	B_2O_3	0,03
	CaO	1,80
L.o.I. at 1050 °C		26,0
Particle size D50 Cilas [µm]		2,6
Particle size D90 Cilas [µm]		9,0

3 Conclusions

Since their introduction in 1996, Dispersing Aluminas have become a true success story as a uniquely performing product line and therefore as a standard in various castable applications. Dispersing Aluminas provide unique features as highly efficient dispersants for the 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. Latest developments i.e. ADS-3 FREE will help to comply with possible regulatory measures in the future. In conclusion this makes Dispersing Aluminas a true "convenience product", therefore providing a significant value addition to modern castable design.

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