

NEW DEVELOPMENTS IN CALCIUM ALUMINATE CEMENTS AND IN DISPERSING ALUMINAS FOR MICROSILICA-CONTAINING CASTABLE SYSTEMS

Doris van Garsel¹, Jeroen v/d Heijden², Rainer Kockegey-Lorenz¹, Gangolf W. Kriechbaum¹

¹Alcoa Industrial Chemicals Europe, Germany; ²Alcoa Nederland B.V., The Netherlands

Abstract

Alcoa's 70% calcium aluminate cements product line, CA-14, has been further improved to fit today's requirements of tight controlled, high performance refractory castables. The improvements are based on the learning's from a recent cement development (CA-270) and result in increased production stability, low water demand clinker plus precisely controlled cement setting through tight cement phase control. The implementation of a new production system gives substantially increased production flexibility. This allowed to generate three distinct CA-14 cements with narrow setting time ranges: CA-14 W (Winter, short setting time), CA-14 M (Medium), CA-14 S (Summer, longest setting time). The water demand in NORTAB testing has been reduced from 12 to 10% while maintaining similar flow properties. Strength values are increased.

The new CA-14 cements match well with other castable matrix products as reactive aluminas or dispersing aluminas. The combination with the new dispersing aluminas for microsilica containing castables (M-ADS 1, M-ADW 1) is shown for a Tabular Alumina T-60 or Mulcoa 60 Chamotte castable. The castables are dispersed at low water contents and their setting times can be steered as desired at varying temperatures (5-20-28°C). - M-ADS/W shows excellent ageing stability. - The influence of different microsilica types on flow and exothermic reaction is demonstrated. The castable performance can be drastically influenced by the selected microsilica quality. Increasing microsilica impurity levels seem to lead to a delayed exothermic reaction.

1. Introduction

The new castable technologies for low moisture self-levelling, vibratable, dry or wet gunning installations require increasingly sophisticated formulations which often contain a broad variety of components. For this systems it is important to select the best suitable cement with a narrow specified setting time in order to keep the system at optimum performance. Alcoa has met this demand with the production of three CA-14 types with controlled setting time ranges. By this for each product a reduced variability of the intrinsic properties is achieved. The products are free of any organic additives which allows the user full freedom in selecting the optimum dispersing aids. *Data on the new CA-14 cements are shown.*

High performance calcium aluminate cement (CAC) is a key component in the Alcoa matrix fines systems (Matrix Advantage System, MAS) for self-flow, vibration, dry and wet gunning concretes. The MAS include, besides the cement, reactive aluminas for self-flowing, vibratable and gunnable mixes as well as dispersing aluminas for vibration and self-flowing castables. The MAS was described in previous publications [1,2]. Dispersing aluminas have two functions: optimum castable dispersion plus steering of cement setting time. They give access to predictable castable setting for alumina based fines (ADS/W) and, newly developed, for microsilica containing fines systems (M-ADS/W). Both are supplied as a pre-mix which allows easy dosage and homogenisation. *Test data for M-ADS/W 1 are shown.* Of interest in this study was the *influence of different microsilicas* on the castable performance.

2. Experimental

The compositions of the selected test castables are given in Tab. 1. Two vibration mixes (Nortab, M-60) and one self-levelling castable (SMS-46) have been used to evaluate cements, dispersing aluminas and microsilica raw material properties. Raw materials other

than supplied by Alcoa Industrial Chemicals Europe are listed in **Tab. 2**. All tests are done in a climatized lab with $20 \pm 1^\circ\text{C}$. All ingredients (including water) are kept at this temperature except otherwise noted. All castables are dry mixed in a Hobart mixer for 1 min, then water is added and time recording is started. Wet mixing time is another 4 min.

Testing in Nortab cement test mortar has been performed according to the Alcoa test methods which are closely related to EN 196 for cement testing [3].

Flow properties of SMS-46 and M-60 are tested with the help of flow cones, dimensions: bottom diameter 100 mm, top 70 mm; 50 mm height for vibration mixes (ASTM cone), 80 mm for self-flow mixes. Flow testing is done after 10, 30, 60, or 90 min (F10, F30, ...). Vibration conditions are 30 sec at a fixed amplitude of 0.5 mm and a frequency of 50 Hz. No vibration is applied for self-flow mixes. The flow diameter is measured after 2 min and averaged from two separate diagonal measurements.

Castable heat development, which results from the exothermic reaction of the cement hydration, is recorded with a thermocouple (type J) which is introduced in 1.5 kg castable put in a closed bucket (hole in cover for thermocouple). The heat development over time is recorded by a datalogger-system supplied by Intab Benelux, NL. Two characteristic points of the temperature curve (*EXO-curve*) can be determined which allow easy and time efficient property evaluation for CC and LCC based castables [1,3]:

- EXO start - time point of 1st temperature rise, correlates with *flow stop & end of workability*
- EXO Max - time point of maximum temperature rise, correlates with *sufficient strength development for demoulding*

3. New CA-14 concept

The traditional CA-14 product line with 70% Al_2O_3 content has been further improved in its concept to fit today's requirements of tight controlled and continuously improved castable performance. To achieve this improvement three steps have been made:

- The implementation of the *learning's from the CA-270 development* (a 70% Al_2O_3 CAC) results in high production stability and low water demand clinker
- The cement setting times are precisely controlled by *tight control of clinker phases*
- The implementation of the "*Alcoa Production System*" (APS) allows to drastically decrease the response time and increase the cement production flexibility.

This allowed to generate 3 cements with distinct ranges of setting time as shown in **Fig. 1**. The former CA-14 M has been separated to two products with short (*CA-14 W*) and moderate setting times (*CA-14 M*). The long setting time of *CA-14 S* remains unchanged. CA-14 cements are *free of any organic additives* which allow full freedom in selecting the optimum dispersing aids.

Test Castables			Nortab	SMS-46	M-60
Tab. Alumina T-60	0.08 - 2 mm	%	80		
	0.02 - 6 mm	%		85	
Chamotte	Mulcoa 60	%			88
Reactive Alumina	CTC 20	%		7	
Microsilica		%		3	5
Cement	CA-14 W/M/S	%	20	5	7
	<i>sum</i>	%	100	100	100
Dispers. Alumina	M-ADS 1	%		0-1	0-1
	M-ADW 1	%		0-1	0-1
Mixing Water	demin.	%	10	4.5	6
	<i>Consistency</i>		VIB	SFL	VIB

Tab. 1: Test Mixes (VIB = vibration, SFL = self-flow)

Raw Material	Type	Producer
Chamotte	Mulcoa 60	CE Minerals, U.S.A.
Microsilica	971 D, 983 U	Elkem, Norway
	RW Füller	RW Silicium, Germany

Tab. 2: Tested chamotte and microsilica types

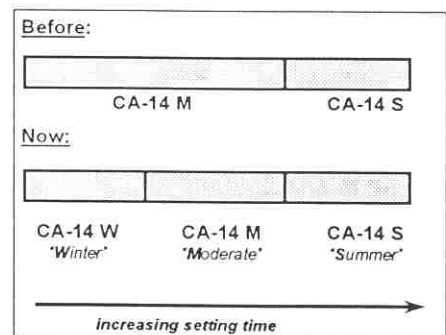


Fig. 1: Previous and new setting time ranges of the CA-14 cement range

The new specifications of the Nortab-based Vicat setting times and vibration flow diameters are shown in Tab. 3. Due to a lower water demand of the cement clinker, the Nortab tests for the improved CA-14 cements are done now with 10% water instead of 12% as previous, giving essentially similar flow values and increased strength values.

Product		CA-14 W		CA-14 M		CA-14 S		old CA-14 M		old CA-14 S	
		min	max	min	max	min	max	min	max	min	max
		10% H ₂ O						12% H ₂ O			
Vicat Setting Time	Initial Setting	min	150	230	320	150	290				
	Final Setting	min	170	250	350	480	350	450			
Vibration Flow	F10	cm	15	15	15	15	16				
	F30	cm	>13	14	14	12	14				
	F60	cm	>12	13	13	11	12				
Flexural Strength (CMOR)	20°C/24h	MPa	> 6				> 5				
	105°C/24h	MPa	> 8				> 5.5				
	1000°C/5h	MPa	> 3				> 1.2				
Crushing Strength (CCS)	20°C/24h	MPa	> 35				> 23				
	105°C/24h	MPa	> 55				> 25				
	1000°C/5h	MPa	> 25				> 15				

Tab. 3: NORTAB test data for water demand, Vicat setting times and vibration flow of previous vs. new CA-14 cements

4. Dispersing aluminas for microsilica containing systems

Two years ago a new approach for the optimum dispersion and set control of microsilica-free, low moisture alumina and alumina-spinel self-levelling castables has been introduced [1, 2]: the Alcoa dispersing aluminas ADS 1, ADS 3 and ADW 1. W stands for Winter and cement setting acceleration, S for Summer and setting retardation. The aluminas can be combined with one another. The products provide optimal dispersion, fast castable wetting and a setting time control of the castable for a wide range of temperatures. The setting can be steered by the adjustment of the of ADSW ratio as required for the individual casting application or ambient temperatures. They can be used in easy dosable amounts of i.e. total 1% for low cement castables. Microsilica-containing mixes with over 0.5% Microsilica additions are not well dispersible with ADSW.

Following the success of this system, a dispersing alumina system for microsilica-containing mixes has been developed: M-ADS 1 and M-ADW 1. Microsilica containing castables have a sensible setting mechanism which is strongly influenced by climatic conditions. Inaccurate dosing of small additive quantities can lead to tremendous influence on placement properties and performance of the castables. Thus also here the concept of pre-mixed ingredients was put successfully in place with the following two dispersing aluminas:

↳ M-ADS 1 - Dispersion & Retardation

↳ M-ADW 1 - Dispersion & Acceleration

Tab. 4 shows the dependencies of M-ADSW-1 ratio and resulting EXO data in the self-flow castable SMS-46 with 4.5% H₂O at low (7°C), moderate (20°C), and high temperatures (28°C). At low placement temperatures M-ADW 1 gives useful results, at moderate conditions various combinations of M-ADS 1 and M-ADW 1 can be used. At elevated temperatures M-ADS 1 is the optimum. Safe working time and strength development is assured at all test temperatures.

Fig. 3 shows the EXO curves of the different M-ADS 1 and M-ADW 1 combinations at 20°C from Tab. 4. The ratio of the dispersing aluminas

Temp.	°C	5	20	20	20	20	20	28
M-ADS 1	%	0	1	0.75	0.5	0.25	0	1
M-ADW 1	%	1	0	0.25	0.5	0.75	1	0
EXO start	min	131	160	115	94	48	22	61
EXO max	min	335	722	398	253	154	105	377

Tab. 4: Steering of EXO times at various temperatures by varying M-ADSW 1 ratios in mix SMS 46 with 4.5% H₂O

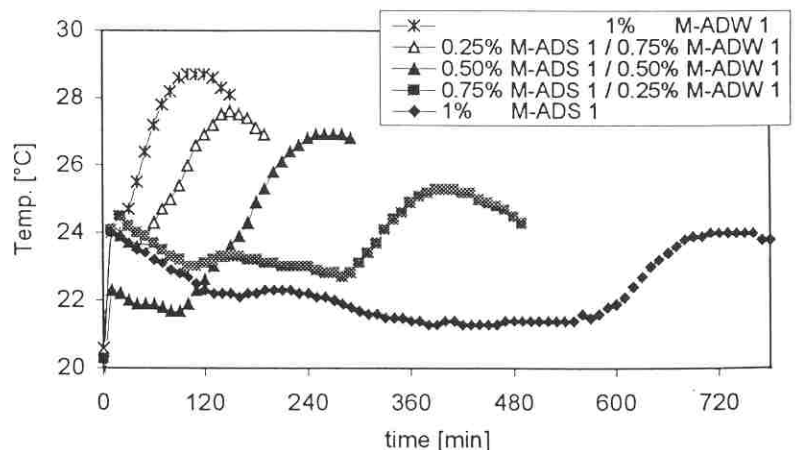


Fig. 3: EXO curves with varying M-ADSW 1 ratios in mix SMS 46 (20°C)

determines the time for flow stop and end of workability (EXO start) and the time of sufficient strength development (EXO max). This can be a useful tool for example in the production of pre-shaped parts to achieve fast setting and demoulding times allowing efficient frequent use of the moulds; or for the installation of larger castable amounts when long setting times are required to prevent layer formation between mix batches.

Another important property is the stability of M-ADS 1 and M-ADW 1 after long time storage. Therefore the *ageing* has been evaluated over a *11 months* time period of storing the separate materials in closed containers. They were tested in 2-3 months intervals in SFL mix SMS-46 for flow and EXO times, used ratio was 0.5/0.5% M-ADS/W 1. The test data showed *no significant ageing behaviour*. An excellent dispersion was observed over the whole time period. A slight trend to shorter setting times was noted by reduced flow and EXO start from 60 to 30-40 min. EXO max values were consistently in the range of 190 min.

Also tested was the ageing in dry *pre-mixes of M-60 castable* with M-ADS/W 1 and with two other established phosphate based dispersants. The mixes were stored *for 4 weeks* in closed containers. After 4 weeks both phosphate based dispersants showed a trend towards extended setting and EXO times and decreased flow. M-ADS/W 1 showed in contrary an advantageous ageing behaviour with slightly shorter setting and EXO start times while keeping similar EXO max times.

5. Influence of different Microsilica Grades on castable flow & setting time (EXO)

With the development of the microsilica dispersing aluminas M-ADS 1 and M-ADW 1, also the influence of typical commercially used microsilica grades on M-ADS/W 1 dispersed mixes was evaluated. Tested were the vibration flow properties and exothermic reactions of test castable M-60 with variations of used 5% microsilica component.

Used microsilica products were 983U and 971D (Elkem, Norway) and RW-Füller (RW Silicium, Germany) in combination with CA-14 W or CA-14 S cements and M-ADS 1 and M-ADW 1. The typical chemical analysis of the three microsilicas, as of product data sheets, is shown in **Tab. 5**. 983 U is the purest of the three products, followed by 971 D, while RW Füller has the highest impurity content. pH values increase in the direction 983U → 971D → RW Füller from acidic to pH neutral.

Tab. 6 shows the test results in M-60 for both CA-14 W and CA-14 S with different constant additions of in total 1% M-ADS/W 1 at a mixing water content of 6%.

producer	Elkem, Norway		RW Silicium, Germany
type	983 U ¹⁾ typ.	971 D ¹⁾ typ.	RW-Füller ²⁾ typ.
SiO ₂ (amorph)	98.3	97.5	95
C	0.4	0.5	1.0
Fe ₂ O ₃	0.05	0.1	0.1
Al ₂ O ₃	0.2	0.4	0.3
CaO	0.2	0.2	0.25
MgO	0.07	0.1	0.4
K ₂ O	0.25	0.3	1.2
Na ₂ O	0.04	0.1	0.15
SO ₃	0.01	0.1	
SO ₄ ²⁻			0.3
sum	1.2	1.8	3.7
pH	5.3	6	7.3

1- data sheet Jan. 93, 2- data sheet 1098

Tab. 5: Typical chemical analysis, pH-data of tested microsilicas (ex product data)

M-60 test mix (VIB)			A	B	C	D	E	F	G	H	I	J	K	L
Microsilica	983 U	%	5			5			5			5		
	971 D	%		5			5			5			5	
	RW-Füller	%			5			5			5			5
Cement	CA-14 W		7	7	7	7	7	7						
	CA-14 S	%							7	7	7	7	7	7
Disp. Alumina	M-ADS 1	%				0.5	0.5	0.5	0.5	0.5	0.5	1	1	1
	M-ADW 1	%	1	1	1	0.5	0.5	0.5	0.5	0.5	0.5			
Mixing Water		%				6	6	6	6	6	6	6	6	6
EXO-Reaction	EXO start	min	17	35	115	49	77	187	77	199	254	163	362	578
	EXO max	min	131	151	270	216	244	435	261	382	1354	555	739	1725
Vibration Flow (ASTM mould)	F 10	mm	140	186	168	193	186	169	194	186	180	189	187	178
	F 30	mm	-	102	161	134	169	165	185	181	177	182	178	172
	F 60	mm	-	-	146	-	100	160	183	180	172	180	182	172

Tab. 6: Tests with different microsilica types in M-60 (20°C)

The *F10* values show for both CA-14 W and CA-14 S and all M-ADS/W 1 additions a *slight decay in the direction 983U → 971D → RW Füller*. EXO start and max times increase in the same direction. EXO max is in all cases the *longest for RW Füller*. An extreme is seen in the combination of CA-14 S with 1% M-ADS 1 (mixes J-K-L), the RW Füller-containing mix L shows an EXO max of 25.5 h, while use of the other two Elkem microsilica results in much shorter times with 9 h for 983U (J) and 10.5 h for 971D (K).

Fig. 4 shows the corresponding EXO curves of the test mixes D-E-F (CA-14 W, 0.5/0.5% ADW/S 1) and Fig. 5 of J-K-L (CA-14 S, 1% M-ADS 1) in M-60. *The strong delay in EXO max for both mixes with RW Füller can be seen.* The EXO curves of both 983 U and 971 D show in both cases a much shorter reaction time and a similar curve shape, with shorter setting for the higher purity microsilica 983U.

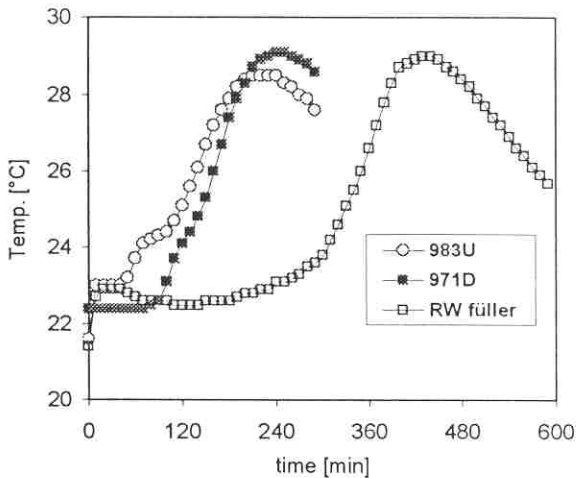


Fig. 4: EXO curve of mixes D-E-F in M-60 (20°C)

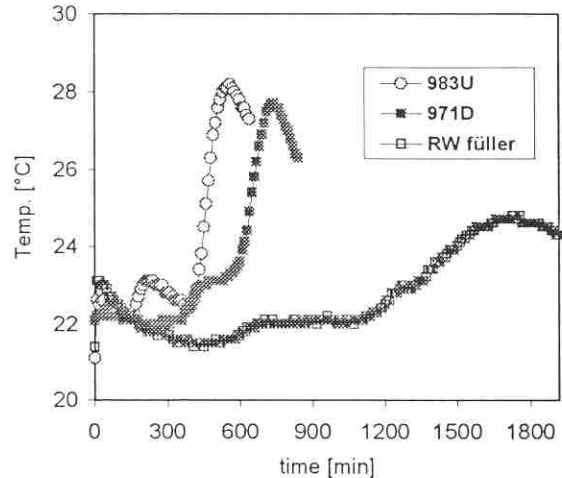


Fig. 5: EXO curve of mixes J-K-L in M-60 (20°C)

→ NOTE different scale of time-axis between Fig. 4 and 5

Based on the described test results a *correlation between microsilica purity and mix performance* in respect to flow and exothermic reaction can be assumed: higher microsilica impurities lead to lesser flow properties and increased exothermic reaction times of cement bonded castables. A possible influence of the increasing pH may also play a role. In the found behaviour.

Therefore special attention to the *castable performance* should be taken when the *microsilica is exchanged* versus another grade in order to maintain a constant castable performance in respect to flow, working time and EXO max. As the later is directly correlating with strength development some strength development differences can be expected.

However, the M-60 test data in Tab. 6 does also show clearly that for the three tested microsilicas *suitable setting times and EXO reactions* can be achieved by combinations of *suitable cements with optimised additions of M-ADSW 1*.

6. Summary

The *new CA-14 concept* provides improved, tight controlled CA-14 cements with narrow setting time ranges. Three different CA-14 cements have been generated: CA-14 W (Winter), CA-14 M (Medium), and CA-14 S (Summer) with fast, medium and slow setting times. In Nortab testing the water addition could be reduced from previous 12% to now 10% while maintaining the flow properties at a similar level and showing increased strength values.

M-ADS 1 and M-ADW 1, the new dispersing aluminas for microsilica containing castables, allow in one step to disperse a castable AND to provide a setting time regulation. The system works safely in microsilica containing self-flowing and vibration castables at low mixing water demands. It is robust and allows adjustments of working time for different applications and climatic conditions, as tested at 5, 20, and 28°C. In all cases a good flow and setting of the castable was provided. An easy dosable addition to castables can be made, i.e. total 1% for

an LCC based on dry mix. This provides a homogeneous distribution of the dispersing alumina in the castable.

M-ADS/W 1 show a beneficial *ageing resistance* and setting behaviour after storage by itself for 11 months or after storage in a pre-mix for 4 weeks. The mixes tend to shorter setting instead of towards longer setting as with conventional phosphate based microsilica dispersants. M-ADS/W 1 can be used in a wide range of castable concepts, i.e. tabular-, chamotte-, bauxite-aggregates containing different microsilicas.

The used *microsilica type can strongly influence* the castable performance. The castable exothermic reaction can be shifted towards much extended duration, while the flow properties are slightly decreased. A possible *correlation between increasing microsilica impurity levels and pH values and observed castable performance* could exist: parallel with increasing impurity/pH levels also decreased flow properties plus increasing exothermic reaction times were observed.

However, the *influence of microsilica changes can be compensated* with the use of *appropriate CA-14 cements and M-ADS/W 1 combinations*

Future investigations should be performed to understand the full impact of the microsilica findings, i.e. tests on the hydration development, strength development of the mixes, correlation to the impurity level and the pH of the raw materials.

7. References

- 1) Kriechbaum, G.W.; Gnauck, V.; Laurich, J.; Stinnessen, I.; Routschka, G.; v/d Heijden, J.: The Matrix Advantage System, a New Approach to Low Moisture LC Self-levelling Alumina and Alumina Spinel Castables, Proc. 39. International Colloquium on Refractories, Aachen, 1996, 211-218
- 2) van Garsel, D.; Kriechbaum, G.W.; Laurich, J.; Gnauck, V.; v/d Heijden, J.: Progress in Refractory Raw Materials for Monolithics, KERMETAL, Kosice/Slovakia, 8.-9.10.1997
- 3) ALCOA calcium aluminate cement test methods brochure, revision 5, 08/99, available through Alcoa Industrial Chemicals Frankfurt