Aging behaviour of Alphabond and Calcium Aluminate Cement bonded castables

Dagmar Gierisch*, Andreas Buhr, Jerry Dutton
Almatis GmbH, Ludwigshafen, Germany

Margarete Hösler, Brunhilde Franz
RHI Urmitz AG & Co. KG, Urmitz, Germany

ABSTRACT

The aging behaviour of factory mixed and packed test castables is investigated by storing in a warehouse for 9 months and under severe conditions in a climate chamber for 4 weeks. Complete bags are also stored in the climate chamber. The castables are tested periodically for mixing behaviour (wet out time), self-flow behaviour, setting start (by ultrasonic device) and strength.

Introduction

The use of the hydratable alumina binder Alphabond 300 has increased dramatically over the past few years. It is used in both cement free castables and in combination with high purity calcium aluminate cement for low (lcc) or ultra low (ulcc) cement castables. In comparison to calcium aluminate cements, Alphabond 300 is more hygroscopic and must be handled with care. When not in use, the product should be stored in sealed packaging in cool, dry conditions.

In the 1990´s extended tests were carried out to investigate the shelf life of Almatis calcium aluminate cements and Alphabond 300 including Brazilian warehouse storage and jungle room conditions in a climate chamber for more severe conditions. Following these tests, a special packaging has been introduced for Alphabond 300. Based upon the results of these tests, a shelf life of 12 months is stated in the Almatis datasheets for both calcium aluminate cements and Alphabond [1,2], if the material is stored under adequate dry conditions.

Dispersion and setting control additives are another component of modern castables which can be susceptible to aging. The shelf life of the Almatis dispersing aluminas ADS/W and M-ADS/W series has also been tested and a shelf life of 12 months is satisfactory if stored under adequate dry conditions.

However, it is well known in the industry, that castables do show aging during storage which can be more or less pronounced depending on the storage conditions and the castable composition. In the case of Alphabond 300 containing castables limited experience was available with regard to aging. This is of particular interest for castables which are to be used for on site installations, and which may be transported and stored for an extended period of time before finally being used for the installation. Therefore this study has been performed and the aging behaviour of different castables has been investigated.

The impact of artificial aging of a 70% alumina cement lab sample on the flow and setting behaviour of EU standard mortars and a silica fume containing low cement castable (lcc) is reported by Mathieu et al. [3]. For the mortar, the flow at 30 and 60 minutes and the setting have already increased after the first days aging of the cement. For the lcc, less additives are required for a pre-aged cement when compared to fresh cement. If the additive package is adjusted based on fresh cement, it might be too much already for cement, which has aged for just a few days. For example the addition of citric acid to increase setting time can considerably reduce the early strength of castables after a few days aging.

The remarkable increase in setting time during aging with citric acid as an additive has also been shown by Krebs [4], who investigated the aging of a medium cement castable containing 70% alumina cement. The pot life of the castable increases even after one day and shows clear differences after eight days, e.g. from 5 to 45 minutes without citric acid and 15 to 210 minutes with 0.02% citric acid.

Parr et al. [5] investigated the aging of a Bauxite based lcc with 70% alumina cement by single component aging and entire castable aging. Due to the complex and interfering aging reactions, the latter is recommended to achieve representative results. The samples have been stored in layers of 25 mm thickness in a climate chamber for up to 60 days. The initial flow and the setting time have been checked, but not the flow at 30 and 60 minutes. The authors distinguish two aging periods - up to 7 days and after 7 days. In the first period, both flow and setting vary but stabilise afterwards. The flow at first increases and later shows a gradual deterioration. The working time increases, and the changes are more marked than the initial flow. After 30 days at 20°C and 70% relative humidity, the castable becomes unsuitable for use.

Sugimoto et al. [6] report differences in aging behaviour of sodium metaphosphate (SMP) and sodium polyphosphate (SPP), both of which are used as dispersing agents in chamotte based low and ultra low cement castables with 70% alumina cement, calcined alumina and silica fume. The test castables have been lab mixed and stored in a climate chamber for up to 60 days. The hardening time was evaluated but not the flow behaviour. SMP retards the hardening by aging, while SPP remains more stable. The increase of hardening time during aging becomes more pronounced with higher silica fume contents and lower cement contents (lcc vs. ulcc). During aging the chains of the SMP are broken up by hydrolysis, which reduces the pH and hampers the cement reaction.

This study will present the results of factory mixed and packed castables, which have been exposed to aging by storage under dry conditions in a warehouse and under defined conditions in a climate chamber, but always as complete bags as initially packed.

Test castables

Four different self-flowing castables based on tabular alumina have been tested for their aging behaviour (table 1):

- LCC-PACA: a low cement castable with polyacrylate/citric acid as additives,
- LCC-ADS/W: with dispersing aluminas ADS 3 and ADW 1 as additives,
- ULCC-M-ADS/W: an ultra low cement castable with dispersing aluminas M-ADS 1 and M-ADW 1 as additives,

Tab. 1. Composition and properties of self flowing test castables at start status

Component	Castable		SFL LCC-PACA	SFL LCC-ADS/W	SFL ULCC-M-ADS/W	SFL NCC-AB
Coarse fraction (up to 6 mm)	Tabular T60/T64	%	70	70	70	70
Fine fraction	T60/T64 -45 MY Li	%	8	8	14	10
	T60/T64 -20 MY	%	7	7		7
Reactive Alumina	CTC 22	%	10	10		10
	CTC 20	%			7	
Silica fume	Elkem 971U	%			5	
Binder	CA-14 M	%	5	5	3	
	Alphabond 300	%			1	3
Additives	Citric Acid	%	0,05			
	Polyacrylate	%	0,05			
	ADS 3	%		0,40		0,75
	ADW 1	%		0,60		0,25
	M-ADS 1	%			0,80	
	M-ADW 1	%			0,20	
Water		%	**5,4**	**4,9**	**4,8**	**4,9**
wet mixing time		min	4	4	4	6
wet out time		sec	15	50	25	50
self flow	10 min	mm	272	286	238	270
	30 min	mm	242	288	248	250
	60 min	mm	no flow	285	244	220
ultrasonic setting start		min	52	62	134	206
CMoR	20°C / 24h	MPa	1	4	4	1
	110°C / 24h	MPa	7	12	15	8
	400°C / 5h	MPa	3	9	14	7
	800°C / 5h	MPa	5	8	16	3
	1000°C / 5h	MPa	3	6	34	1
	1500°C / 5h	MPa	18	32	53	29
	1650°C / 5h	MPa	26	43	63	39
CCS	20°C / 24h	MPa	4	17	15	3
	110°C / 24h	MPa	36	60	93	27
	400°C / 5h	MPa	38	66	108	44
	800°C / 5h	MPa	37	71	77	30
	1000°C / 5h	MPa	24	27	145	6
	1500°C / 5h	MPa	93	116	143	83
	1650°C / 5h	MPa	128	165	166	102

- NCC-AB: a no cement castable with Alphabond 300 and ADS 3 and ADW 1 as additives.

The castable matrix contains T60/T64 -45 µm LI and/or -20 µm and the reactive aluminas CTC 22 or CTC 20 in combination with silica fume. All formulations were adjusted to give satisfactory flow values at 10 and 30 minutes and a start of setting below 240 minutes.

Test conditions

500 kg of each test castable were dry mixed and packed in 25 kg valve-sealed bags (multi-layer: paper-plastic foil-paper) at RHI Urmitz. The fresh material was shipped to the Almatis plant in Ludwigshafen and stored in a warehouse tent. Storing under dry conditions was guaranteed, but castables were exposed to seasonal temperature variations. Before testing the material, the particular bags were stored in the air conditioned lab at 20°C for temperature acclimatisation. Within one week the castables were tested in the Ludwigshafen lab for wet out time, flow behaviour up to 60 minutes, ultrasonic setting start and strength after various pre-firing temperatures (table 1).

The castable was wet mixed in batches of 5 kg using a Hobart A 200 planetary mixer at speed 1 for 4 minutes (LCC`s and ULCC) and 6 minutes (NCC). The wet out time was determined as described in a previous paper [7]. The flow properties after 10, 30 and 60 minutes (F10, F30, F60) were measured by the cone test (lower diameter 100 mm, upper diameter 70 mm, height 80 mm). The setting behaviour was measured by ultrasonic equipment. The eight channel device records the velocity of ultrasound through the sample during the curing time by means of a transmitter and a receiver (figure 1). The hardening of the test piece gives an increase in velocity and the initial setting coincides with the first rise in the velocity vs. curing time graph (figure 2).

An overview of storage conditions and test intervals are shown in table 2. A new unopened bag was always used for each test. The castable properties were tested at a constant water demand. The test series will continue until the castables become unusable or the test material is consumed. Also a series of tests were performed in a climate chamber (HEKK 2057 S from Weiss Enet B.V./NL, volume 500 l) using complete unopened bags. Here different settings were chosen to compare with the warehouse aging trend.

Tab. 2. Test conditions during storage in warehouse and climate chamber and test intervals

	warehouse	climatic cabinet		
	changing conditions	75% / 35°C	85% / 35°C	95% / 35°C
storage	warehouse tent, dry	climatic cabinet (unopened bag)	climatic cabinet (unopened bag)	climatic cabinet (unopened bag)
treatment	seasonal temperature variations	rel. humidity 75% temperature 35°C	rel. humidity 85% temperature 35°C	rel. humidity 95% temperature 35°C
test intervals	start status 1 month 3 months 5 months 7 months 9 months	start status 1 week 2 weeks 4 weeks	start status 1 week 2 weeks 4 weeks	start status 1 week 2 weeks 4 weeks

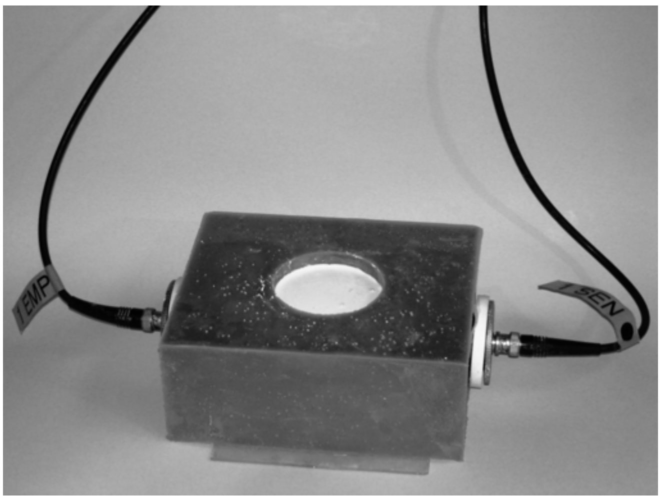

Fig. 1. Eight channel ultrasonic device - sample carrier with transmitter and receiver

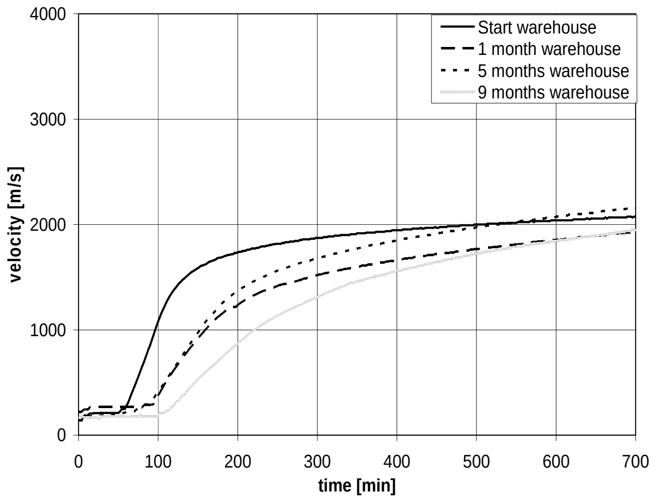

Fig. 2a. Ultrasonic graphs of LCC-PACA / warehouse storage

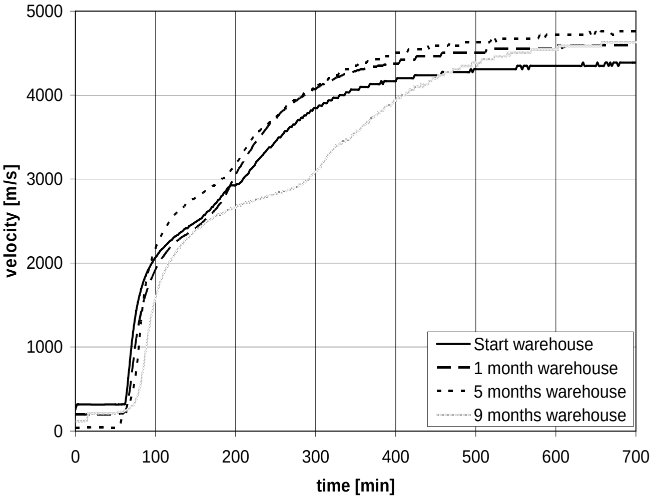

Fig. 2b. Ultrasonic graphs of LCC-ADS/W / warehouse storage

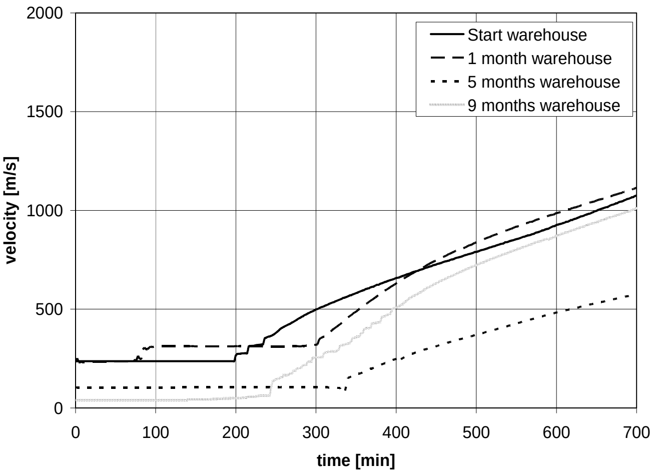

Fig. 2c. Ultrasonic graphs of NCC-AB / warehouse storage

Results and discussion

The results of the warehouse aging up to 9 months are given in table 3 and the impact of aging on the flow behaviour (F30) is represented in figure 3.

The test castables can show some variation in results during the testing periods. These are not considered to be due to aging unless the specific values are confirmed by later results (e.g. from tests performed 2 months later). For example, low flow values of ULCC-M-ADS/W were noted after one month, but in the later tests a reasonable flow behaviour was once again achieved. One reason for this observation may be a slight bag to bag variation, which may be more pronounced for the ULCC in comparison to other castables due to the very low cement content.

Also it has been accepted that there can be some variation of the ultrasonic setting start without attributing that as a result of aging unless a trend becomes clear. However, these variations are not seen as technically critical unless the workability period for the installation of the castable would become too short or the setting of the castable delayed too much. Only LCC-ADS/W shows a very stable setting start at about 60 +/- 10 minutes.

LCC-PACA has a water demand of 5.4% and shows a very fast wet out at the start. After 9 month warehouse storage the wet out is achieved at about 90 seconds instead of 15, which was achieved initially. The same trend towards longer wet out after aging occurs in the climate chamber particularly at 95% rel. humidity. LCC-PACA shows no flow at 60 minutes when fresh material is used. The flow at 10 and 30 minutes remains relatively stable over a period of 5 to 7 months, although a slight decrease after 7 months storage shows a deterioration of flow which results in no flow after 9 months. The castable is still usable but only at a 0.4% higher water demand. The decrease in flow corresponds to the results obtained from test castable stored under extreme conditions in the climate chamber, where the castable is no longer usable after 2 weeks at 85% or 95% rel. humidity.

A slight decrease of setting start is observed. The corresponding ultrasonic graphs are shown in figure 2a. Here, the warehouse results do not correlate with the climate chamber, which shows the reverse trend.

Strength properties remain stable over the whole period. Even with the increased water demand the strength values are still at the same level. At 75% rel. humidity and 35°C no change in strength is observed over a period of 4 weeks, but at 85% rel. humidity the strength is reduced by about 50% after 2 weeks storage. For both, 85 and 95% relative humidity, the castable is unusable after 2 weeks.

LCC-ADS/W requires less water when compared to LCC-PACA (4.9 v.s 5.4%) and achieves an even better flow. It shows a very stable performance over 9 months warehouse storage. Wet out time for the warehouse material is about 50 seconds whereas in the climate chamber at 85% rel. humidity a rise in wet out of up to 100 seconds is observed. The only exception to the extremely good flow of about 290 mm is the F60 value (no flow) at 7 months. This can be explained by the setting start, which in this case was adjusted to about 60 minutes. By contrast aging in the climate chamber at 85% rel. humidity reduces the flow (F30) down to no flow after 4 weeks.

The setting start at about 60 minutes in the warehouse aging remains very stable up to 9 months (figure 2b). The climate chamber (85 and 95% rel. humidity) shows a trend towards shorter setting times during aging, which has not yet been observed in the warehouse testing. With regard to strength no change for both warehouse and climate chamber occurs.

ULCC-M-ADS/W shows aging stability, if the above mentioned variations of the test results are not attributed to aging reactions. The wet out shows a slight increase from 25 to 50 seconds after 9 months, which is still fast. The flow varies at different test periods, but no trend attributable to aging is shown. The same applies for the setting behaviour, where the setting start varies between 100 and 200 minutes. In the climate chamber at 95% rel. humidity the flow decreases (no F30 after 1 week) and the setting gets shorter. The castable becomes unusable after 4 weeks at 85% and 95% rel. humidity.

NCC-AB achieves a wet out time between 50 and 80 seconds over the whole test period up to 9 months. In the climate chamber the wet out remains stable until the castable becomes unusable after 4 weeks at both, 85 and 95% rel. humidity. The flow shows a slight increase after 1 month but afterwards remains stable at a high level of about 300 mm. More severe climate chamber conditions of 85% rel. humidity and upwards show a trend towards a decrease in flow, which is more pronounced at 95% rel. humidity. This probably indicates an aging behaviour which may occur in the warehouse at a later stage.

The setting time of Alphabond bonded castables can be recorded by the ultrasonic method as shown in figure 2c. This would not be possible with the EXO method [7]. Compared to both LCC´s (figure 2 a and b) NCC has not reached the plateau of stable velocity after 700 min, and it still keeps rising at 1200 minutes, where the test ends. However, the strength achieved after 24 hours curing and after drying is comparable to LCC-PACA, but lower when compared to LCC-ADS/W and ULCC-M-ADS/W. The setting start remains stable within a range of 200 to 350 minutes and shows no clear trend in the warehouse aging. In the climate chamber it shows no change at 75% rel. humidity, but at 85% at first an increase is seen, followed by a decrease, and at 95% a decrease is observed. Once again, an aging trend may be indicated, which has not yet been shown in the warehouse aging.

Tab. 3. Castable properties from start status up to 9 months warehouse storage

LCC-PACA			Start	1 month	3 months	5 months	7 months	9 months
water demand		%	5,4	5,4	5,4	5,4	5,4	**5,4 / 5,8**
wet out time		sec	15	40	40	15	60	90 / 90
self flow	10 min	mm	272	255	271	270	228	**no flow** / 218
	30 min	mm	242	228	253	233	198	**no flow** / 211
	60 min	mm	no flow	no flow	no flow	no flow	no flow	**no flow** / 175
ultrasonic setting start		min	52	96	106	72	164	102 / n.d.
CMoR	20°C / 24h	MPa	1	n.d.	1	n.d.	1	n.d.
	110°C / 24h	MPa	7	n.d.	8	n.d.	8	n.d.
	800°C / 5h	MPa	5	n.d.	7	n.d.	6	n.d.
LCC-ADS/W								
water demand		%	4,9	4,9	4,9	4,9	4,9	4,9
wet out time		sec	50	60	60	30	40	40
self flow	10 min	mm	286	307	305	300	299	296
	30 min	mm	288	300	293	291	292	282
	60 min	mm	285	298	260	272	**no flow**	253
ultrasonic setting start		min	62	62	54	58	64	62
CMoR	20°C / 24h	MPa	4	n.d.	5	n.d.	4	n.d.
	110°C / 24h	MPa	12	n.d.	10	n.d.	16	n.d.
	800°C / 5h	MPa	8	n.d.	12	n.d.	11	n.d.
ULCC-M-ADS/W								
water demand		%	4,8	4,8	4,8	4,8	4,8	4,8
wet out time		sec	25	25	30	35	70	45
self flow	10 min	mm	238	170	185	204	203	211
	30 min	mm	248	146	183	217	204	217
	60 min	mm	244	155	183	206	211	208
ultrasonic setting start		min	134	92	174	130	198	124
CMoR	20°C / 24h	MPa	4	n.d.	4	n.d.	4	n.d.
	110°C / 24h	MPa	15	n.d.	13	n.d.	13	n.d.
	800°C / 5h	MPa	16	n.d.	18	n.d.	20	n.d.
NCC-AB								
water demand		%	4,9	4,9	4,9	4,9	4,9	4,9
wet out time		sec	50	50	80	50	70	80
self flow	10 min	mm	270	315	315	310	299	294
	30 min	mm	250	302	302	283	297	294
	60 min	mm	220	296	285	263	293	279
ultrasonic setting start		min	206	304	214	340	296	252
CMoR	20°C / 24h	MPa	1	n.d.	1	n.d.	1	n.d.
	110°C / 24h	MPa	8	n.d.	8	n.d.	14	n.d.
	800°C / 5h	MPa	3	n.d.	5	n.d.	4	n.d.

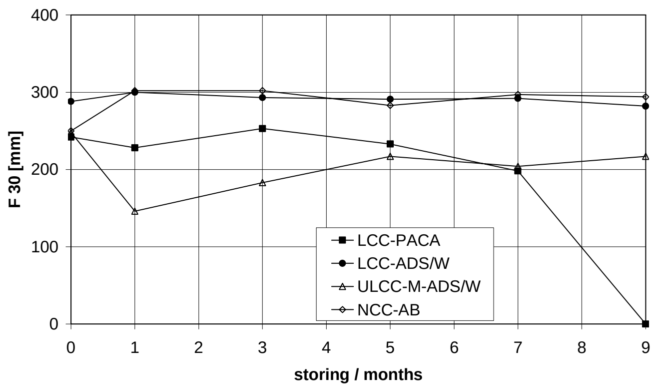

Fig. 3. Impact of warehouse aging on flow at 30 minutes

Summary

The comparison between the climate chamber conditions at 35°C and the warehouse aging shows, that 75% rel. humidity is not strong enough to indicate aging trends within 4 weeks. However, 95% rel. humidity is very severe and can show strong effects even after 1 week. Therefore 85% rel. humidity seems the most suitable condition in order to accelerate the aging process and indicate aging trends for the castables.

All castables except LCC-PACA have not reached their shelf life after 9 months storing in the warehouse. The shelf life of the LCC with dispersing aluminas ADS/W is higher when compared to the additive system polyacrylate + citric acid. This becomes unusable after 2 weeks in the climate chamber at 85% rel. humidity compared to 4 weeks for LCC-ADS/W.

The NCC with Alphabond 300 and dispersing aluminas ADS/W shows an aging resistance which is comparable to the LCC-ADS/W. This is an important result, because it shows, that Alphabond bonded castables do not require the special packaging of the pure Alphabond binder to achieve a reasonable shelf life.

The ULCC with dispersing aluminas M-ADS/W also shows a high aging resistance, even under demanding conditions in the climate chamber at 85 and 95% rel. humidity. But the variation of test results between these tests, where new bags were always used, is higher when compared to the other castables.

Future evaluations will show if longer aged warehouse material will show the same aging trend as under the demanding conditions exhibited in the climate chamber.
No investigations have been done with regard to aging mechanism, during this project.

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