THE VALUE OF ADDITIVES IN REFRACTORY CASTABLES – INDUSTRIAL CASTABLE AGING TRIALS

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ABSTRACT

The aging behaviour of dry low cement castables with silica fume and different organic and inorganic additive systems has been investigated. Castables were produced and packed under industrial conditions and were stored in dry conditions, typical for the industry, for twelve months. All castable mixes were regularly tested by flow tests, and for setting behaviour and strength development. The results show some aging taking place in all castables, but to a different degree depending upon the additive system used. The retardation of the cement hydration reaction is less pronounced for the dispersing alumina system when compared to the phosphate additive systems, especially when in combination with citric acid. When accepting cement hydration times of up to 18 hours, the dispersing alumina castable gives a shelf life of 12 months whereas castables with sodium tripolyphosphate provide only three months. The polyphosphate castable would achieve 12 months if citric acid were not used to overcome flow decay problems which show after four months of aging.

INTRODUCTION

Dispersion and setting control additives are components of modern refractory castables. They can be susceptible to aging and can interact with other castable components, e.g. calcium aluminate cement binders, during storage. Such interaction between additives and binders can influence workability, setting behaviour and also strength development.

Aging resistance is a requirement additives have to fulfil in refractory castables [1]. However, castable aging limits the storage time of dry mixed and packed castables. Therefore a shelf life is given by the castable suppliers. For modern low and ultra-low cement castables, a shelf life of 6 months is usually guaranteed. For very critical compositions it can be limited to only 4 months, but if a castable shows higher aging stability, then the shelf life can be extended to up to 12 months. Also, as ambient conditions impact the aging behaviour, material should at least be stored under adequate dry conditions in order not to accelerate the aging process.

In a previous study the aging behaviour of warehouse-stored industrially packed castables was investigated by Gierisch et al. [2]. The paper included comparison between a low cement castable containing dispersing alumina ADS/W and ultra-low cement castable with M-ADS/W. Both additives systems showed storage stability over a period of 9 months as reported in the paper. The test series was continued and subsequent measurements confirmed storage stability over 12 months, and showed stable flow and setting (figure 1). For the silica fume containing castable with M-ADS/W, a higher variation of results was observed without showing a trend attributable to aging.

Short term aging was investigated by Schnabel et al. [3] for silica fume castables comparing different additive systems, e.g. dispersing aluminas M-ADS/W, sodium tripolyphosphate (STPP) and sodium hexametaphosphate (SHMP) with and without citric acid. Aging behaviour was tested over a period of 14 days by open storage at 20°C and 65% relative humidity. The castable containing 1% M-ADS/W achieved an early EXO Max which remained stable over the test period. Comparable behaviour was observed for the mix with 0.1% STPP. The castable with SHMP showed a slight increase in setting over time. The addition of citric acid to the phosphate additive castables resulted in a long EXO Max at the start, which was further retarded over the storage period. Such a marked increase in setting time during aging with citric acid as an additive has also been shown by Krebs [4].

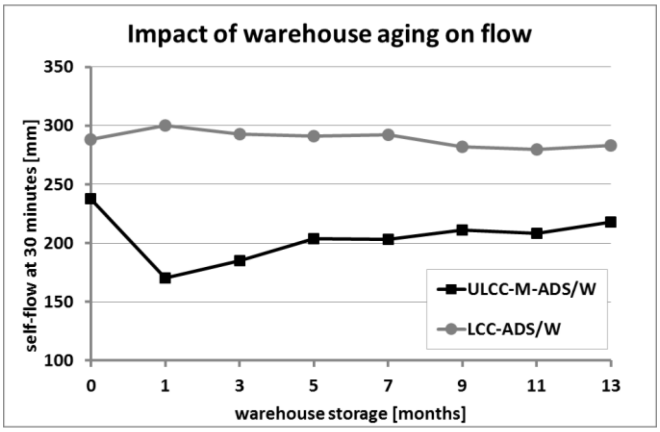


Fig. 1: Impact of warehouse storage on self-flow at 30 minutes of LCC with ADS/W and ULCC with M-ADS/W

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 which is comparable to storage at the supplier and on-site.

EXPERIMENTAL

Test castables

Five different additive systems have been tested for their short and long term aging behaviour in a silica fume containing low cement vibration castable based on tabular alumina (table 1):

Tab. 1: Composition of vibration test castables.

Component	Castable		VIB DA	VIB STPP	VIB STPP-CA	VIB PP	VIB PP-CA
Tabular T60/T64	- 6 mm	%	82	82	82	82	82
Alumina	CT 9 FG	%	8	8	8	8	8
Silica fume	U 971	%	5	5	5	5	5
Cement	CA-14 M	%	5	5	5	5	5
Additives	M-ADS 1	%	0,5				
	M-ADW 1	%	0,5				
	Sodium tripolyphosphate	%		0,1	0,1		
	Polyphosphate 8	%				0,05	0,05
	Citric Acid	%			0,03		0,03
Water		%	**4,5**	**5,0**	**5,0**	**5,0**	**5,0**

VIB-DA: castable with dispersing aluminas M-ADS 1 and M-ADW 1 as additives.

VIB-STPP: with sodium tripolyphosphate as additive.

VIB-STPP/CA: formulation containing sodium tripolyphosphate and citric acid.
VIB-PP: using polyphosphate as additive system with a pH value of about 8.
VIB-PP/CA: mixture with polyphosphate and citric acid as additives.

The castable matrix contains T60/T64 -45 µm LI and calcined alumina CT 9 FG in combination with 5% silica fume. All formulations were adjusted to give satisfactory flow values at 10 and 30 minutes.

Test conditions
300 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. Due to the time needed for transport, the first test was carried out with material which was already one week old (starting point).
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, exothermal reaction (EXO) and strength after various pre-firing temperatures. During the study it was decided not to use the ultrasonic method for evaluation of setting behaviour. Ultrasonic curves can be misinterpreted when a stiffening reaction takes place prior to the cement reaction. In previous projects it became obvious, that the stiffening reaction of castables containing phosphate additives is sufficient to increase the ultrasound velocity significantly but cannot be correlated to any real strength development [3]. The EXO measurement provides reliable data for the strength development.
A new unopened bag was always used for each test. The castables were wet mixed in batches of 5 kg using a Hobart A 200 planetary mixer at speed 1 for 4 minutes. The castable properties were tested at a constant water demand of 4.5% for VIB-DA and 5.0% for the castables containing phosphate additive. The test intervals of the short and long term aging are shown in table 2.

Tab. 2: Test conditions during storage and test intervals.

		warehouse
storage		dry
treatment		seasonal temperature variations
test intervals	short term	1 week = starting point 2 weeks 4 weeks
	long term	2 months 3 months 4 months 5 months 6 months 8 months 10 months 12 months

Results and discussion
The results of the warehouse aging up to 12 months are summarised in table 3.
At the beginning of each test interval the particle size distribution (PSD) of the respective bags was checked by wet sieve analysis. Industrially produced test castables show some variation in PSD, e.g. about 10% for the fraction < 63µm, when comparing single bag analyses. As PSD impacts castable properties such as wet out and flow, some variation in castable results during the testing period are likely. These are not considered to be due to aging unless the specific values are confirmed by subsequent results (e.g. from tests performed 1 or 2 months later). However for practical use the bag-to-bag variation can be considered as less critical as almost always more than one bag is used for a mixing batch and any differences tend to offset each other.

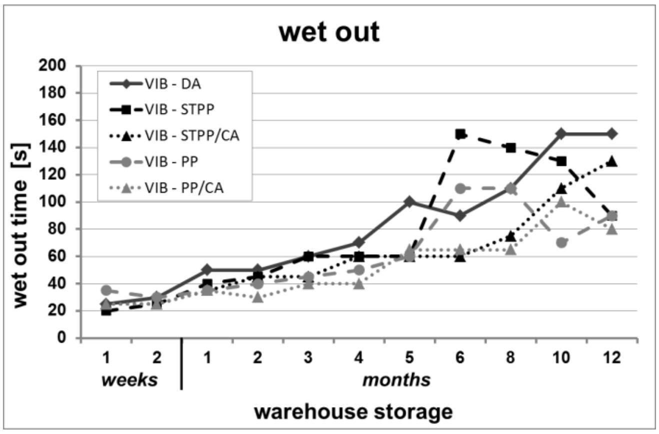


Fig. 2: Impact of warehouse aging on wet out time.

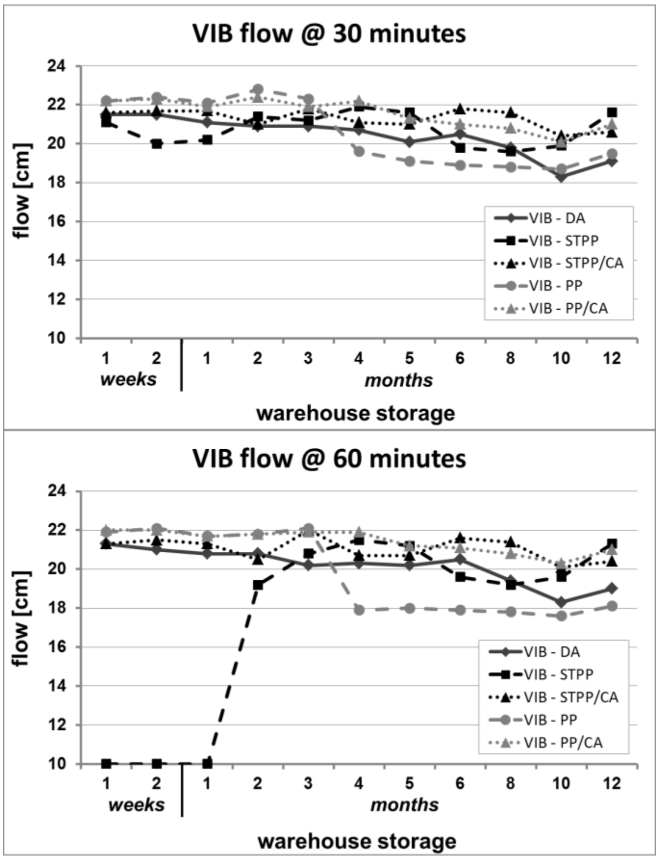
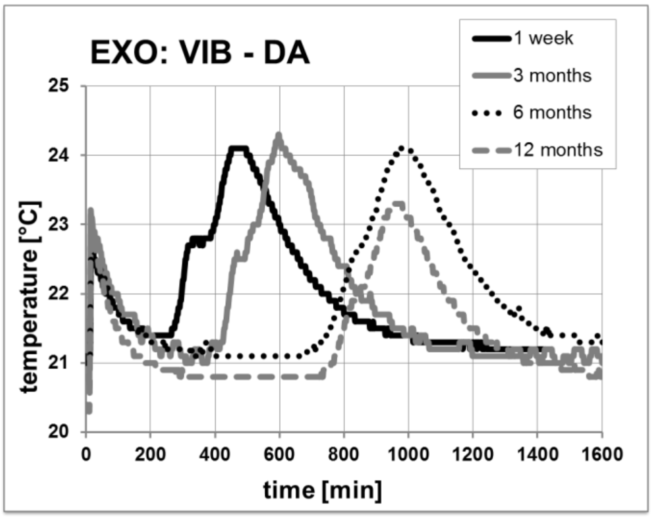


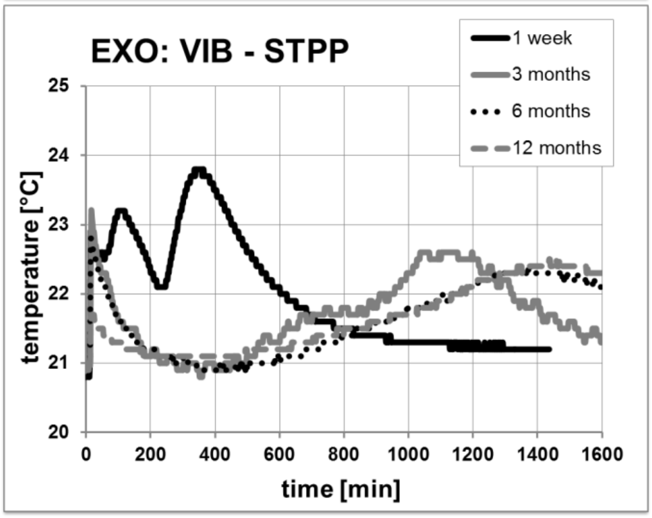
Fig. 3 a-b: Impact of warehouse aging on flow at 30 and 60 minutes.

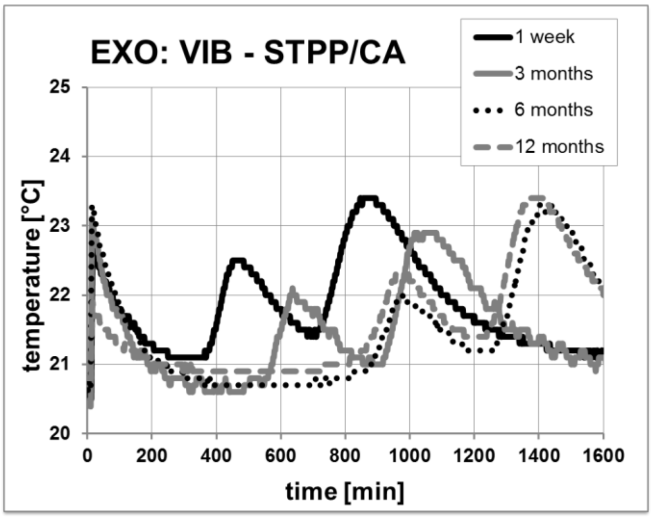
Tab. 3: Castable properties from starting point up to 12 months warehouse storage; VIB-DA 4.5% mixing water, all phosphate additive castables 5.0%.

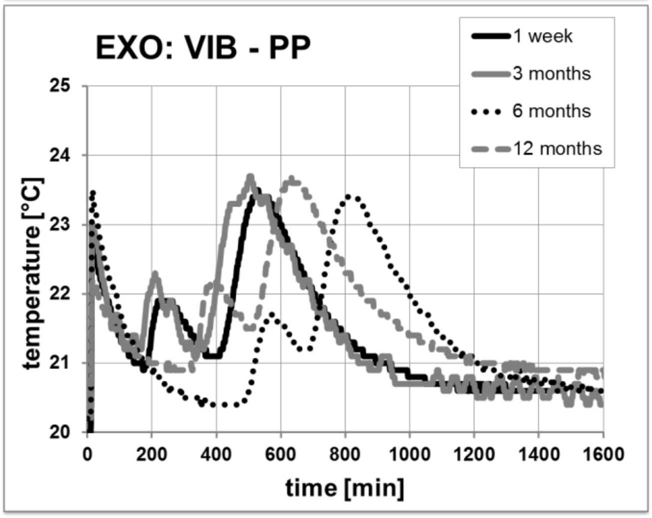
			weeks		months								
VIB-DA			1	2	1	2	3	4	5	6	8	10	12
wet out time		sec	25	30	50	50	60	70	100	90	110	150	150
vibration flow	10 min	cm	21,6	21,4	21,0	21,1	21,0	20,9	20,4	20,7	20,0	18,9	19,2
	30 min	cm	21,5	21,5	21,1	20,9	20,9	20,7	20,1	20,5	19,8	18,3	19,1
	60 min	cm	21,3	21,0	20,8	20,8	20,2	20,3	20,2	20,5	19,4	18,3	19,0
EXO Max		h	7,9	7,9	7,6	8,1	9,9	10,8	14,0	16,4	16,3	17,2	16,0
CCS	20°C / 24h	MPa	30	34	34	27	48	44	50	41	37	37	46
	110°C / 24h	MPa	127	132	134	129	158	147	163	135	131	131	149
	350°C / 5h	MPa	137	147	134	134	151	134	161	143	127	156	161
	1000°C / 5h	MPa	266	279	291	249	255	250	236	211	230	207	241
VIB-STPP													
wet out time		sec	20	25	40	45	60	60	60	150	140	130	90
vibration flow	10 min	cm	22,4	22,4	22,3	22,1	21,6	22,0	21,7	20,1	20,0	20,0	21,6
	30 min	cm	21,1	20,0	20,2	21,4	21,2	21,9	21,6	19,8	19,6	19,9	21,6
	60 min	cm	no flow	no flow	no flow	19,2	20,8	21,5	21,2	19,6	19,2	19,6	21,3
EXO Max		h	5,8	5,7	5,6	6,9	18,5	22,3	20,6	22,9	21,5	22,3	24,2
CCS	20°C / 24h	MPa	32	33	31	31	43	39	40	31	32	26	26
	110°C / 24h	MPa	114	118	112	109	126	108	114	109	100	96	86
	350°C / 5h	MPa	115	117	107	104	114	105	102	98	89	100	78
	1000°C / 5h	MPa	235	258	248	219	238	225	213	206	216	212	192
VIB-STPP/CA													
wet out time		sec	25	25	35	45	45	60	60	60	75	110	130
vibration flow	10 min	cm	21,8	21,8	21,7	21,0	22,3	21,1	21,0	21,9	21,6	20,6	20,7
	30 min	cm	21,6	21,7	21,7	21,0	21,8	21,1	21,0	21,8	21,6	20,4	20,6
	60 min	cm	21,3	21,5	21,3	20,5	22,0	20,7	20,7	21,6	21,4	20,1	20,4
EXO Max		h	14,5	14,9	15,3	15,4	17,6	20,7	23,4	23,7	23,4	23,7	23,2
CCS	20°C / 24h	MPa	37	36	36	40	43	42	45	38	39	32	40
	110°C / 24h	MPa	121	118	116	131	119	133	133	113	105	106	117
	350°C / 5h	MPa	124	116	105	132	111	122	124	102	92	105	117
	1000°C / 5h	MPa	264	261	248	270	214	260	257	218	209	227	243
VIB-PP													
wet out time		sec	35	30	35	40	45	50	60	110	110	70	90
vibration flow	10 min	cm	22,4	22,6	22,3	22,8	22,8	21,8	20,7	20,0	20,1	20,1	20,6
	30 min	cm	22,2	22,4	22,1	22,8	22,3	19,6	19,1	18,9	18,8	18,7	19,5
	60 min	cm	21,9	22,1	21,7	21,8	22,1	17,9	18,0	17,9	17,8	17,6	18,1
EXO Max		h	8,8	8,8	8,7	7,4	8,4	8,1	12,6	13,6	12,2	10,7	10,5
CCS	20°C / 24h	MPa	38	36	37	36	37	37	41	36	38	32	36
	110°C / 24h	MPa	130	111	120	111	115	120	119	119	125	100	110
	350°C / 5h	MPa	132	108	109	100	102	110	105	101	111	123	113
	1000°C / 5h	MPa	234	208	217	207	210	227	224	214	236	192	220
VIB-PP/CA													
wet out time		sec	25	25	35	30	40	40	65	65	65	100	80
vibration flow	10 min	cm	22,4	22,5	22,2	22,6	22,2	22,6	21,7	21,4	21,1	20,5	21,2
	30 min	cm	22,2	22,3	21,9	22,4	21,9	22,2	21,3	21,0	20,8	20,1	21,0
	60 min	cm	22,0	22,0	21,7	21,8	21,9	21,9	21,2	21,1	20,8	20,3	21,0
EXO Max		h	31,0	32,2	35,5	33,1	43,2	51,8	72,0	81,6	72,0	75,6	73,2
CCS	20°C / 24h	MPa	20	20	11	36	21	14	21	10	9	5	7
	110°C / 24h	MPa	105	100	120	104	104	81	101	97	79	82	83
	350°C / 5h	MPa	94	88	112	88	94	73	94	74	65	90	83
	1000°C / 5h	MPa	211	208	239	185	211	173	208	174	161	166	182

VIB-DA is mixed at a low water demand of 4.5% whereas all phosphate containing test castables require 5.0%. The impact of aging on the wet out time and flow behaviour (F30 and F60) is represented in figures 2 and 3 a-b. Even with the lower water demand for VIB-DA, the same short wet out as for the other castables is achieved at the start. After 5 to 6 months a change in wet out is observed for all mixes. VIB-STPP and VIB-PP show a higher increase in wet out than castables with citric acid. After 12 months the biggest increase is observed for VIB-DA. The wet out is achieved at about 150 seconds instead of 25, which was achieved initially. Here the lower water addition might be the reason for the more pronounced difference. In order to compare VIB-DA with the other castables 12 months old material was additionally mixed with 5.0% water. Wet out of 80 seconds is comparable to phosphate containing mixtures after the same storage period.
Flow properties at 30 minutes (F30) remain stable for all vibration castables up to 3 months. Afterwards VIB-PP shows a decrease in flow values from 22.3 to 19.6 cm and stays at this level. VIB-DA shows a slight downward trend in F30 values from 20 – 21 cm to 18 – 19 cm after 10 months storage. These trends are also seen for flow at 60 minutes. The only exception is VIB-STPP which behaves differently during the first months of storage by showing no flow at 60 minutes. After 2 months of aging normal flow is achieved. If a longer working time is required for the mix with STPP as additive, a retarding agent has to be added, e.g. citric acid. Citric acid does not only influence the working time but at the same time has an impact on other properties such as setting time.
Exothermal reaction after 1 week, 3, 6 and 12 months storage is chosen to represent the impact of aging on setting behaviour (fig. 4 a-e). 1 week storage represents the starting point. After 3 months the first trends in setting behaviour are observed and 6 – 12 months represents the typical shelf life guaranteed by monolithic suppliers.









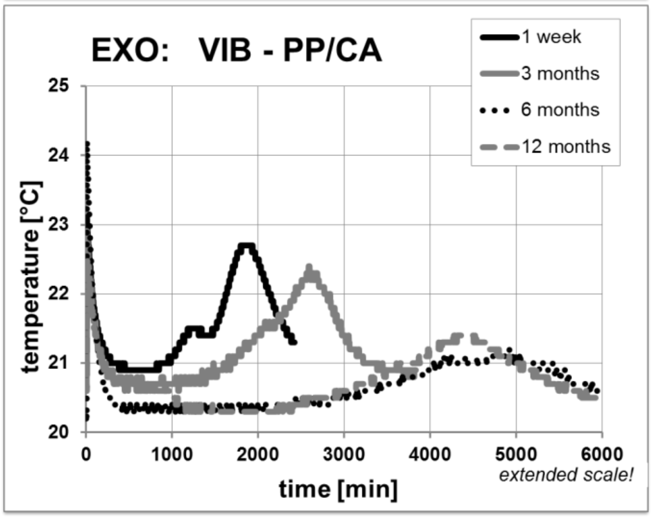


Fig. 4 a-e: EXO graphs of test castables after 1 week, 3, 6 and 12 months warehouse storage.

VIB-DA was adjusted to a working time of 4 and EXO Max of about 8 hours for the starting point. A minor shift in EXO Max to later times occurs after 3 months storage. After 6 months storage the time for EXO Max has doubled to 16 hours. Later, the setting behaviour remains stable. Even with the delay in setting time during the first half of the storage period the shape of the EXO curve remains the same showing a well-defined maximum temperature peak. Setting within 24 hours is ensured over the entire storage period and the castable is usable even after 12 months.
Vibration castable with STPP as additive already shows a strong increase in setting time after 3 months and another shift after 6

months storage time. Within half a year EXO Max is delayed by more than 17 hours. In addition to the extension of setting time, there is a broadening and flattening of the maximum temperature peak. This indicates a less pronounced and predictable cement reaction and strength development. Also ultrasound measurements, which are not discussed in this paper, show a change in shape of the curve comparable to the EXO method. The weaker cement hydration reaction together with the EXO Max being close to 24 hours can become very critical for lining installations. VIB-STPP/CA initially shows a longer setting time than VIB-STPP. An addition of only 0.03% citric acid extends EXO start from 1 to 6 hours and maximum from 5.8 to 14.5 hours. As for the other test castables the aging effect occurs within the first 6 months. Even with the longer setting in the beginning of the aging study, EXO Max is around 24 h, comparable to VIB-STPP.

VIB-PP shows some variation in EXO times over the entire test period. The change in EXO Max is less than for the castables containing sodium tripolyphosphate and similar to VIB-DA. However, VIB-PP shows a flow decay at F30 and F60 after 4 months of aging. When citric acid is added as a retarder to enhance the working time, the aging behaviour changes dramatically. A citric acid dosage of only 0.03% increases the time for EXO Max by 22h to about 31h. These setting times are considered to be too long for almost all applications and can easily result in failures during installation e.g. slumping of the lining or introduction of cracks when the former is removed. During storage the setting is further retarded to more than 3 days after 6 months and EXO curve flattens over time.

No aging effect is observed within the first weeks of storage. However, the start material used for the project was already 1 week old and therefore aging within the first days of storage could not be investigated.

Strength properties were tested for all castables at different temperatures (20°C/24h, 110°C/24h, 350°C/5h and 1000°C/5h). VIB-DA always achieves strength which is comparable to or higher than for the phosphate containing mixes. Due to the ultra-long setting of VIB-PP/CA, 24h-green strength is very low. At 110°C VIB-PP/CA gains in strength and is therefore only slightly below the strength of all other test castables. Further hydration takes place at 110°C due to the hydrothermal condition which prevails in the castable test piece [1]. Strength values at 350°C are comparable to the level achieved for 110°C “dried” strength. Strength after firing at 1000°C is substantially influenced by silica fume fines and therefore not discussed in detail. Variation is within the normal range. Green and dried strength are presented in figure 5 a-b.

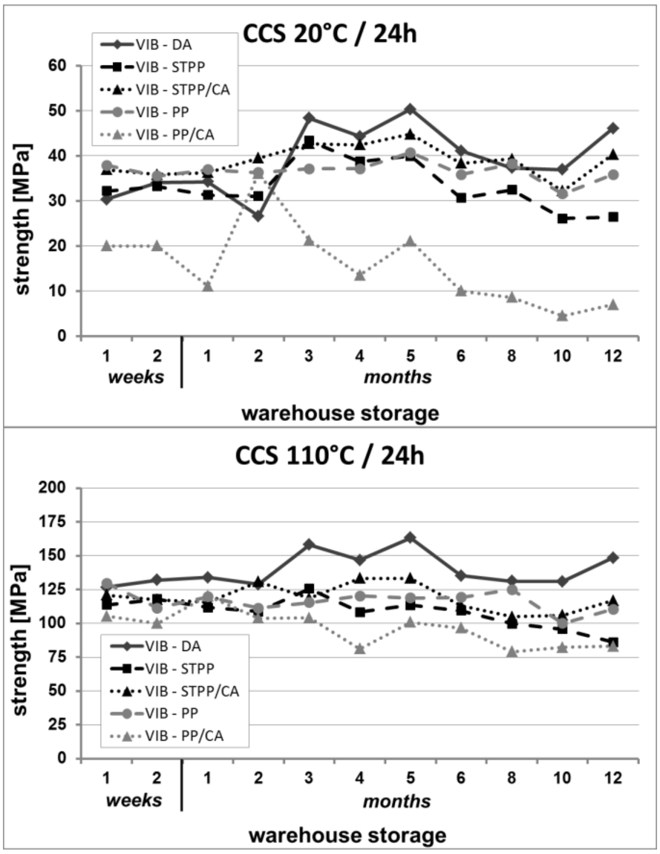


Fig. 5 a-b: Impact of warehouse aging on green and dried strength.

SUMMARY

An aging trend is observed for all additive combinations tested in a silica fume castable. However, the aging of VIB-DA containing M-ADS/W remains within more narrow limits when compared to VIB-STPP, -STPP/CA and -PP/CA. This is particularly the case for setting behaviour. EXO Max stays well below 24 hours over the entire storage period and ensures strength development sufficient for de-moulding and handling activities. VIB-PP also shows a less severe shift in EXO. However, if the working time has to be adjusted to more than 30 minutes a retarder must be added and setting time and aging behaviour strongly deteriorates as shown for VIB-PP/CA. The short working time of phosphate containing castables is caused by a stiffening reaction of phosphate in combination with cement. This reaction can be retarded by small additions of citric acid taking into account that the main cement reaction and the start of strength development are strongly retarded. Small additive dosages, as in the case of citric acid, always include the risk of overdosage and insufficient homogenisation which negatively affects the placing properties. As a result the risk of installation failures rise.

Castables containing Dispersing Aluminas, both ADS/W and M-ADS/W, do not show stiffening. The end of working time correlates with the beginning of strength development. In addition, Dispersing Aluminas offer dispersion at low water demand, easy adjustment and control of working and setting time and improved castable properties. A low cement castable containing ADS/W shows aging stability after storage for over 1 year. Also a mix with M-ADS/W is still usable after storage for 12 months as the aging trend within the first 6 months is moderate and stabilisation is achieved after. Therefore ADS/W and M-ADS/W provide better aging resistance when compared to phosphate/citric acid systems and a higher reliability when working on-site with material which had been stored for some time in the warehouse.

Short-term aging behaviour within the first week could not be covered within this test series. Such investigation would have to be started immediately after dry mixing and packing on-site.

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