MOISTURE PICK UP AND STRENGTH OF HYDRAULICALLY BONDED PRE-CAST SHAPES

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ABSTRACT

Hydraulically bonded pre-cast shapes can pick up moisture during storage. This has an impact on the mechanical strength. This paper investigates and compares test castables with two different hydraulic binders, calcium aluminate cement and calcia free hydratable alumina. Test bars are dried at different temperatures and stored in air under ambient lab conditions for up to six months. The weight increase as result of moisture pick up and the impact on cold modulus of rupture and cold crushing strength are determined. Additional packaging as protection against moisture pick up is also tested. The results provide a data base for the magnitude of strength reduction which could be expected and tolerated during storage of pre-cast shapes under industrial conditions.

Introduction

Alphabond is a hydratable alumina, which is used as a binder in non-cement castables, e.g. in steel ladle and other applications. The market interest in this calcia free hydraulic binder has increased considerably in the last decade. It is used in both castables and pre-cast shapes, where improved slag resistance and hot properties are required or in special refractory lining applications which cannot tolerate any CaO content. The general properties of Alphabond have been summarised in a previous paper [1]. The aging behaviour of dry mixed Alphabond and calcium aluminate cement bonded castables has been reported in another paper [2].

It is well known in the industry, that calcium aluminate cement bonded pre-cast shapes do show moisture pick up during storage which can be more or less pronounced depending on the pre-firing temperature, storage conditions and the components used in the formulation. For Alphabond bonded pre-cast shapes, limited experience was available with regard to moisture pick up and a resulting strength reduction. This is of particular interest as pre-cast shapes have to be transported and normally are stored for some period of time before they are finally installed and used. Therefore test bars of Alphabond castables and a low cement castable are investigated for comparison purposes in this study.

Routschka et al. [3,4] investigated in detail in an extended test series the impact of moisture pick up on strength of cement bonded castables. Test bars dried at 110°C and fired ≥ 1000°C were stored up to one week either in air or in a climate cabinet. The moisture pick up takes place after a very short storage period. First effects were observed after six hours and a significant moisture pick up was determined after one day. For example a tabular alumina castable with a cement content of 15% showed a moisture pick up of 0.085% after 24 hours storage in air. This resulted in a 17% lower cold crushing strength. As a result of the study it is shown that a moisture pick up of only 0.02% already has an impact on strength. Additional tests showed that the loss of strength is reversible when re-drying the stored test bars. With regard to the pre-firing temperature (1000-1500°C) it was shown that the moisture pick up dropped with rising pre-firing temperatures and remained very low when pre-fired at high temperatures, even after a longer storage period. Routschka [5] also discussed a high deviation in strength results within inter-laboratory tests, which is partly caused by different storing conditions in the participating laboratories.

Within the scope of these previous studies the test bars were dried at 110°C and fired at 1000 to 1500°C. The moisture pick up after treatment at intermediate temperatures was not investigated. Under industrial conditions pre-cast shapes are normally dried at 300 to 500 °C before being packed and shipped to the customer. This treatment removes the main part of the chemically bonded water, and enables an easier and faster heating up in end use when compared to in situ installed castables. Therefore the moisture pick up and strength development of pre-cast shapes after drying at intermediate temperatures of 200, 350, and 450°C and storing for up to six months is of particular interest and has been investigated in this paper.

Test castables

Four different tabular alumina based vibration castables were tested; three no cement castables (NCC´s) with hydratable alumina and one low cement castable with 70%Al_2O_3 calcium aluminate cement (table 1):

- VIB AB: NCC with 3% Alphabond 300,
- VIB AB-F: NCC with 3% Alphabond 300, 0.5% silica fume and spinel containing E-SY 2000
- VIB AB-F-M: NCC with 3% Alphabond 300, 0.5% silica fume, and 2.5% dead burned magnesia (spinel forming) and E-SY 2000
- VIB CAC: LCC with 5% CA-14 M.

The matrix of the silica fume free castable VIB AB contains tabular alumina T60/T64 -20MY and / or -45MY

Li in combination with reactive alumina CL 370. The silica fume containing castables contain reactive alumina/ spinel E-SY 2000 and alumina rich spinel AR 78 -45MY. All formulations were adjusted to a normal working time of about 1 hour by dispersing alumina ADS/ADW.

In addition test bars of different binder pastes have been investigated to show the storage effects and check the phase composition at different drying temperatures:

- AB: an Alphabond 300 paste with water demand of 100% (water/binder ratio of 1),
- AB-F: an Alphabond 300 paste with 8% silica fume and water demand of 100%,
- CAC: a CA-14 M paste with water demand of 45% (water/binder ratio of 2.2)

Tab. 1. Composition of vibration test castables and Cold Modulus of Rupture of fresh and aged test bars

Castable / Component			VIB AB	VIB AB-F	VIB AB-F-M	VIB CAC
Coarse fraction (up to 6 mm)	Tabular T60/T64	%	75	75	75	75
Fine fraction	T60/T64 -45 MY Li	%	2			
	T60/T64 -20 MY	%	7			7
	AR 78 -45 MY	%		5	5	
Reactive Alumina	CL 370	%	13			13
	E-SY 2000	%		16,5	14	
Silica fume	Elkem 971 U	%		0,5	0,5	
Magnesia dead burned DIN 70	China MgO 90%	%			2,5	
Binder	Alphabond 300	%	3	3	3	
	CA-14 M	%				5
Additives	ADS/W	%	1	1	1	1
Water		%	**4.4**	**4.0**	**4.6**	**4.4**
CMoR 200°C / 5h	fresh	MPa	16	14	9	20
	1 month	MPa	16	14	9	21
	3 months	MPa	15	13	9	19
	6 months	MPa	12	10	7	17
CMoR 350°C / 5h	fresh	MPa	21	24	11	23
	1 month	MPa	16	20	8	18
	3 months	MPa	17	20	8	18
	6 months	MPa	15	16	7	18
CMoR 350°C / 5h vacuum packed	fresh	MPa	21	24	11	23
	1 month	MPa	21	20	11	23
	3 months	MPa	19	20	8	23
	6 months	MPa	16	16	8	22
CMoR 450°C / 5h	fresh	MPa	12	21	10	19
	1 month	MPa	9	17	6	14
	3 months	MPa	11	n.d.	n.d.	15
	6 months	MPa	11	n.d.	n.d.	16

Test procedure

The castables were mixed in 5 kg batches using a Hobart A 200 planetary mixer at speed 1. Dry mixing took one minute and wet mixing four minutes. Test bars (40mm x 40mm x 160mm) were cast and de-moulded after 14 to 24 hours. Immediately after de-moulding the test bars were treated at different test temperatures in the drying furnace. For drying at 200°C test bars were heated up within 90 minutes and dried for 24 hours at that temperature. For bars dried at 350°C and 450°C the test bars were heated up for 610 and 660 minutes and dried for five hours at final temperature.

Immediately after drying the samples were weighed and strength tests were performed with sample temperature still above 100°C to avoid any moisture pick up. The remaining test bars were stored in the lab in air under ambient conditions for one, three, and six months. After the defined storage periods the weight increase and strength were determined. The percentage weight increase is always given in relation to the initial weight. The Cold Modulus of Rupture (CMoR) was tested for up to six months. The Cold Crushing Strength (CCS) was tested after one month.

For moisture protection, test pieces dried at 350°C were packed in plastic bags (figure 1). Impact of re-drying after storage was investigated by measuring the strength after storage for one month with and without re-drying at the previous treatment temperature.

Test bars from binder pastes were produced in the same way as for the castables, by mixing one kg batches for one minute dry and four minutes wet. After temperature treatment the samples were crushed into lumps to provide a higher surface area making them more susceptible to moisture absorption and stored in air in the laboratory. Half the 350°C samples were packed in plastic bags before storage. In addition to the weight increase, the mineralogical phase composition was determined by X-ray diffraction at the German Refractory Institute (DIFK /Bonn).

Fig. 1. Test bar packed in plastic bag for moisture protection

Results and discussion

All test bars show some strength decrease after storage regardless whether Alphabond or cement is used as the binder (table 1 and figure 2 for CMoR and table 3 for CCS). The amount of strength loss depends on the castable composition, the pre-treatment temperature, and the storage time. For a six month storage period the CMoR reductions are in the range of 15 to 36%. The cement bonded VIB CAC shows lower strength loss (15-22%) when compared to the Alphabond bonded VIB´s 25-36%. The only exception is VIB AB pre-dried at 450°C which shows only 8% CMoR reduction after six months. However, the overall strength level of this castable after drying at 450°C is considerably lower when compared to those dried at 200 or 350°C (12 vs. 16 and 21MPa). Therefore drying at 450°C seems, in general, not to be recommended for Alphabond bonded pre-cast shapes. Only the VIB AB-F does not show the strength loss after 450°C drying. The small amount of silica fume addition has a clear impact here.

The overall strength level of the Alphabond VIB´s AB and AB-F is comparable to that of the VIB CAC when dried at 200 or 350°C. But the magnesia containing VIB AB-F-M has a 40-50% lower strength level. Therefore such strength losses for spinel forming castables could become more critical for practical applications. This would depend upon the starting strength level. In the industry, 4 MPa CMoR and 30 MPa CCS are often considered minimum strength levels for the handling and installation of pre-cast shapes.

Tab. 2. Cold crushing strength of fresh and aged test bars (1 month)

CCS			VIB	VIB	VIB	VIB
pre-drying	storage		AB	AB-F	AB-F-M	CAC
200°C / 5h	fresh	MPa	114	141	71	97
	1 month	MPa	69	91	47	75
350°C / 5h	fresh	MPa	158	183	98	191
	1 month	MPa	83	115	53	130
350°C / 5h plastic bag	fresh	MPa	158	183	98	191
	1 month	MPa	114	123	60	142
450°C / 5h	fresh	MPa	104	203	103	173
	1 month	MPa	68	118	56	101

For all test castables the strength after drying at 350°C is the highest when compared to drying at 200 or 450°C. However the weight increase due to moisture pick up is higher and the resulting strength loss is more in relative terms. The major strength loss occurs after one month´ storage, after that time the strength decreases only slightly (figure 2). For samples dried at 200°C changes in strength are only shown after three to six months.

The weight increase of samples dried at 200°C is in the range of 0.1 to 0.4%, and it is about 50% lower for VIB CAC when compared to the Alphabond VIBs (table 3). The longer the storage period, the higher the moisture absorption. For samples dried at 350°C the weight increase is about 0.4% after one month for all test castables and the changes afterwards are minimal. At 450°C, only VIB AB and VIB CAC have been tested. The Alphabond castable shows a moisture pick up of below 0.1%, whereas the cement castable shows about 0.2% moisture pick up.

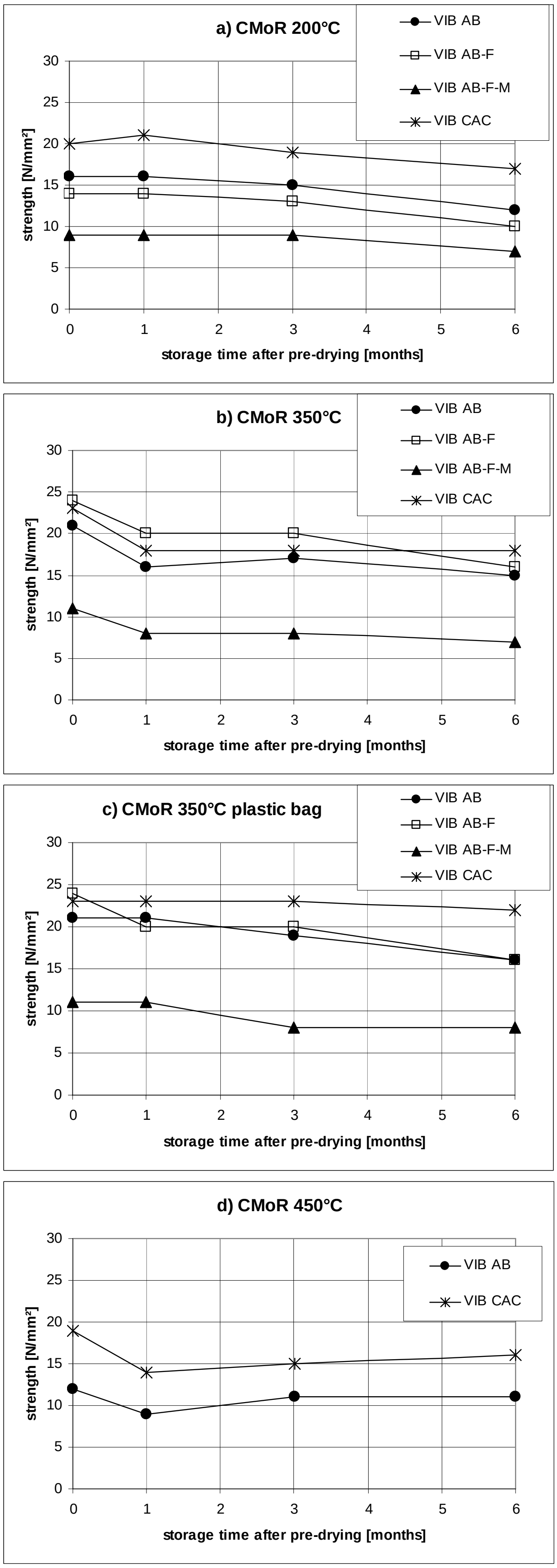

Fig. 2 a-d. Castable test bars: Development of Cold Modulus of Rupture during storage period

Tab. 3. Weight increase of aged castable test bars

weight increase			VIB	VIB	VIB	VIB
pre-drying	storage		AB	AB-F	AB-F-M	CAC
200°C / 5h	1 month	%	0.14	0.24	0.25	0.12
	3 months	%	0.24	0.25	0.27	0.15
	6 months	%	0.30	0.42	0.33	0.18
350°C / 5h	1 month	%	0.43	0.43	0.43	0.34
	3 months	%	0.40	0.41	0.42	0.43
	6 months	%	0.45	0.44	0.55	0.48
350°C / 5h plastic bag	1 month	%	0.02	0.05	0.04	0.02
	3 months	%	0.05	0.02	0.03	0.04
	6 months	%	0.10	0.08	0.07	0.05
450°C / 5h	1 month	%	0.08	n.d.	n.d.	0.20
	3 months	%	0.07	n.d.	n.d.	0.17
	6 months	%	0.09	n.d.	n.d.	0.17

In order to investigate the aging behaviour of pre-cast shapes under moisture protection, test bars dried at 350°C were packed into plastic bags and stored for up to six months. The results in figure 3 (and table 3) clearly show that packing in a plastic bag considerably reduces the moisture pick up, although some weight increase is still detected (0.05 to 0.1% after six months). The CMoR decrease during storage is reduced by packing in a plastic bag and occurs later (after three or six months).
The practicality of protecting pre-cast shapes in such a way will depend upon specific situations - how long the pieces will be stored before installation, or what mechanical stresses may occur during transportation or installation. Shrink wrapping of a pallet of pre-cast shapes will provide protection until the pallet is opened. Then the normal aging process will apply to unused pieces if they are not all used at the same time. Shrink wrapped protection of each piece may be ideal but may not be feasible in normal industrial circumstances.

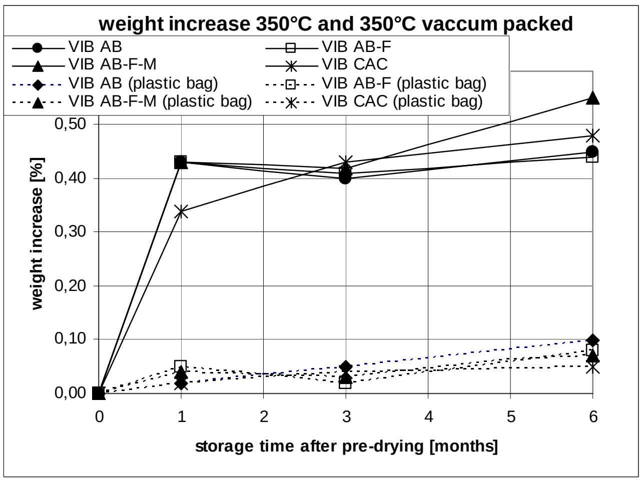

Fig. 3. Weight increase of castable test bars after drying at 350°C, with and without plastic bag protection. Weight increase as a result of moisture absorption during storage is reduced by plastic bag packaging

Routschka et al. [3,4] have shown that re-drying test bars after storage increases the strength back to the original level. This also applies in the practical application of pre-cast shapes when the lining is exposed to heat and to high temperatures during use. However, for the transportation and installation of pre-cast shapes, the strength the pieces exhibit after moisture absorption is what really counts. If this strength was too low, damage to the pieces could occur. The effect of re-drying the test pieces has also been checked in this investigation and the results are given in table 4. The results of Routschka et al. can be confirmed. All pre-dried test bars which have been exposed to air for one month will regain the initial strength when re-dried at the same temperature as before.

Tab. 4. Impact on strength of re-drying aged test bars

CMoR			VIB	VIB	VIB	VIB
pre-drying	storage		AB	AB-F	AB-F-M	CAC
200°C / 5h	fresh	MPa	16	14	9	20
	1 month	MPa	16	14	9	21
	re-drying 200°C	MPa	16	15	8	21
350°C / 5h	fresh	MPa	21	24	11	23
	1 month	MPa	16	20	8	18
	re-drying 350°C	MPa	20	24	11	22
450°C / 5h	fresh	MPa	12	21	10	19
	1 month	MPa	9	17	6	14
	re-drying 450°C	MPa	14	22	10	20
CCS			VIB	VIB	VIB	VIB
pre-drying	storage		AB	AB-F	AB-F-M	CAC
200°C / 5h	fresh	MPa	114	141	71	97
	1 month	MPa	69	91	47	75
	re-drying 200°C	MPa	114	143	75	108
350°C / 5h	fresh	MPa	158	183	98	191
	1 month	MPa	83	115	53	130
	re-drying 350°C	MPa	156	190	96	185
450°C / 5h	fresh	MPa	104	203	103	173
	1 month	MPa	68	118	56	101
	re-drying 450°C	MPa	138	194	100	171

The amount of binder in the test castables is low. This is typical for most of the industrially produced pre-cast shapes. It would be difficult to further investigate the specific changes in the binder phase during storage in air on the basis of the whole castable mix. Therefore, pieces of pure binder pastes have been prepared and also stored for up to six months (table 5). In general, the weight increase is the highest for the pieces pre-dried at 350°C. This is in line with the results of the castable test bars (table 3).
Both Alphabond binder pastes (with and without silica fume) show an abnormal weight increase with a higher weight increase after a shorter storage time whereas a lower weight increase is seen after longer storage times

(figure 4). The effect is most obvious for the pure Alphabond paste after pre-drying at 350°C (figure 4a): after one month storage the weight increases by 13.1% but after six months only by 7.8%. Some of the initially absorbed moisture must have been released between one and six months. The silica fume containing paste AB-F also shows about 50% less weight increase after six months storage when compared to one and three months (figure 4b). This behaviour is not observed in any of the test castable bars. After pre-drying at 450°C the weight increase of the Alphabond paste is much lower when compared to that at 200 and 350°C. The weight increase is around 2%.
The cement binder paste shows normal behaviour, where the moisture absorption increases as storage time increases. The main increase has already taken place after one month (figure 4c). After six months storage the weight increase is of the same magnitude as for the Alphabond pastes (around 7-9%). The weight increase after pre-drying at 200°C is only very small and stays below 1% after six month storage.
For all binder pastes packed in a plastic bag the moisture absorption is reduced to below 2% even after six months.

Tab. 5. Weight increase of aged binder paste test bars

weight increase			binder paste		
pre-drying	storage		AB	AB-F	CAC
200°C / 5h	1 month	%	5.1	5.6	0.5
	3 months	%	5.6	6.6	0.7
	6 months	%	3.8	3.6	0.6
350°C / 5h	1 month	%	13.1	6.8	5.5
	3 months	%	8.6	7.6	7.8
	6 months	%	7.8	3.5	8.6
350°C / 5h plastic bag	1 month	%	0.3	0.3	0.3
	3 months	%	1.0	1.3	1.0
	6 months	%	1.0	1.7	0.8
450°C / 5h	1 month	%	2.7	n.d.	4.8
	3 months	%	1.7	n.d.	6.2
	6 months	%	2.0	n.d.	6.9

In order to investigate the mineralogical phase changes during moisture pick up, the binder pastes AB and CAC have been X-rayed soon after drying at 200, 350, and 450°C, and again after one month storage.
The phase composition of the Alphabond paste changes depending upon the pre-drying temperature (figure 5). At 200°C sharp Bayerite $Al(OH)_3$ peaks occur, and Boehmite AlOOH is also seen with wider peaks, indicating a less ordered crystal phase (pseudo-Boehmite). Khi-Al_2O_3, a transition alumina is the third component. At 350°C, the Bayerite has decomposed and changed to pseudo-Boehmite. Khi-alumina and gamma-alumina are the other phases. At 450°C, no water containing crystal phase can be found. Only the non hydratable transition alumina phases khi-alumina and gamma-alumina are seen. This explains the low weight increase of the Alphabond castable and paste during storage after pre-drying at 450°C, because no reaction partner for the water is present. After 200°C, the Alphabond binder is less susceptible to weight increase

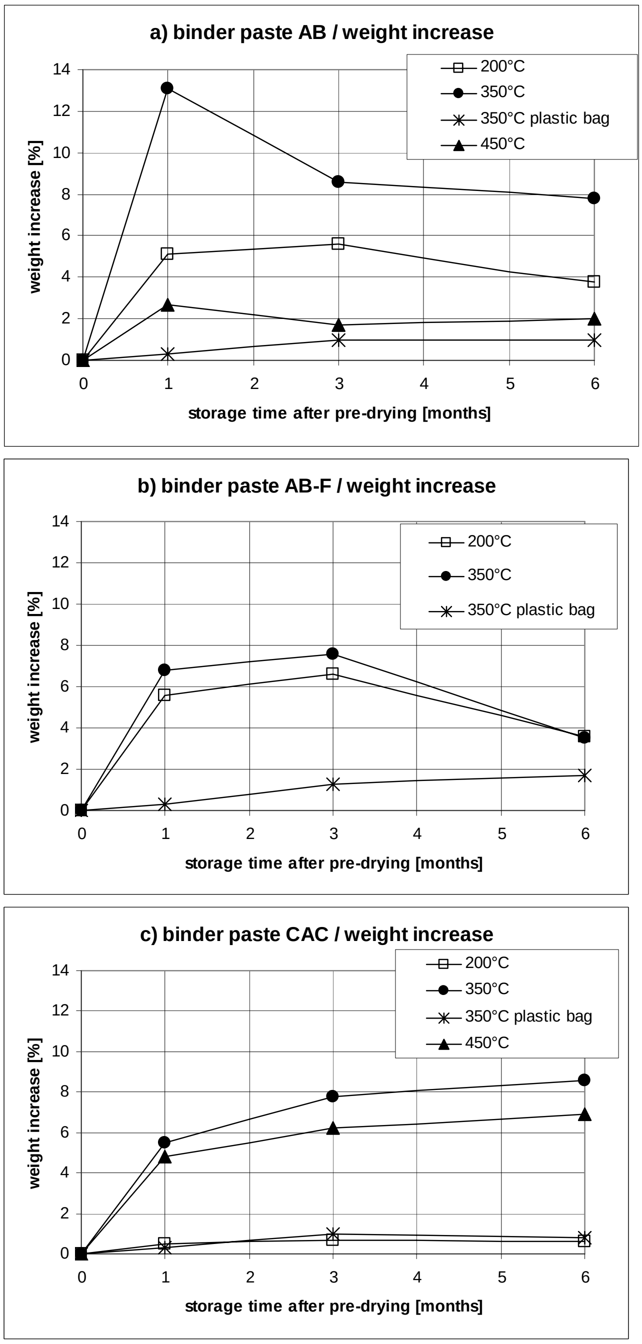

Fig. 4a-c. Binder paste test bars: Development of weight increase during storage period

and moisture pick up, because Bayerite is already a fully hydrated phase. The poorly crystallised pseudo-Boehmite phase is obviously much more susceptible to moisture pick up, because the samples at 350°C show the highest weight increase. Interestingly, and in spite of the considerable moisture pick up at 350 and 200°C the samples after 1 month storage do not show changes in the X-ray diagram when compared to the fresh samples. If new phases were formed they must be all amorphous.
The X-ray results of stored AB paste cannot explain the abnormal weight increase behaviour mentioned above. Further investigations by differential thermal analysis and thermogravimetry will be necessary here, but they were not within the scope of this study.

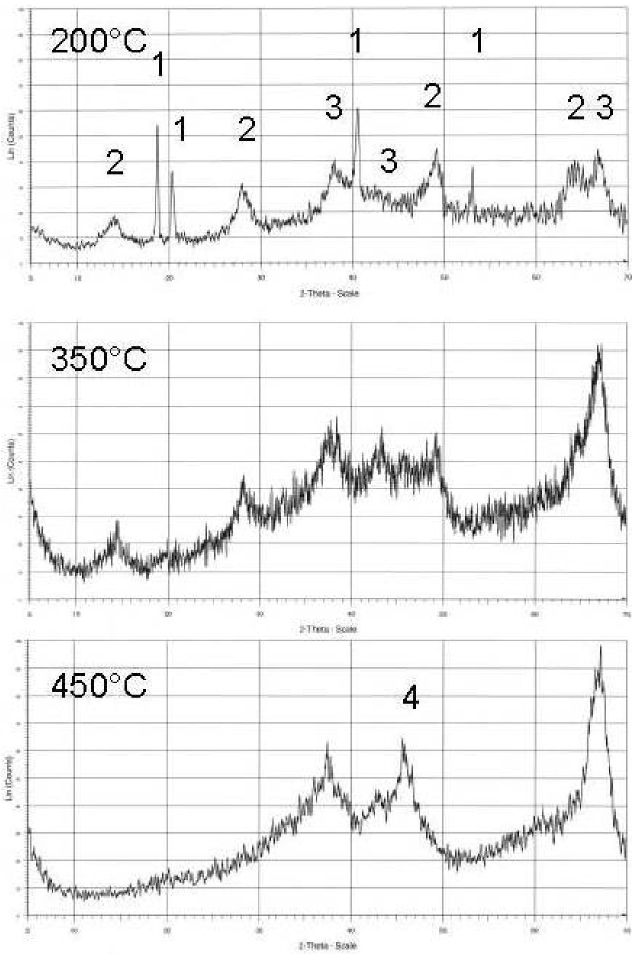

Fig. 5a-c. X-ray diffraction (5-70 degree 2-theta) from Alphabond binder paste pre-fired at 200, 350, and 450°C (5 hours each).
1 = Bayerite $Al(OH)_3$, 2 = Boehmite AlOOH, 3 = khi Al_2O_3, 4 = gamma Al_2O_3.
No Bayerite at 350°C; no Boehmite at 450°C; khi Al_2O_3 already at 200°C, much more at 350°C; gamma Al_2O_3 at 450°C (minor at 350°C).

The CAC paste phase composition by X-ray diffraction shows some changes between samples dried at 200 and 450°C. At 200°C, Katoite $Ca_3Al_2(OH)_{12}$ and Grossite $CaAl_4O_7$ are the main phases and Gibbsite $Al(OH)_3$, $CaAl_2O_4$, and Corundum are minor phases. The Katoite is starting to decompose in the sample dried at 350°C and becomes a minor phase. The other phases are unchanged. At 450°C, Gibbsite is decomposed and the Katoite peaks become very small. No changes can be observed by X-ray in the samples after one month storage.

Conclusion

In general Alphabond pre-cast shapes show a comparable behaviour to cement bonded pre-cast shapes with regard to moisture pick up during storage and the consequential strength reduction. At a pre-drying temperature of 350°C the weight increase is the highest for both binders. However, the overall strength level is also the highest with pre-drying at this temperature. They behave differently when comparing the susceptibility to moisture pick up at pre-drying temperatures of 200 and 450°C. Alphabond pre-cast shapes show a higher moisture pick up at the lower drying temperature (200°C), whereas cement pre-cast shapes are more susceptible after 450°C.
The amount of strength loss depends upon the castable composition, the pre-treatment temperature, and the storage time. Within this study the strength loss after six months storage in air was in the range of 15-36% when compared to fresh samples. The amount of strength loss of the cement bonded test bars was about 30% lower when compared to the Alphabond test bars. The composition of the Alphabond test castables has a major impact on the overall strength level. Small additions of silica fume enhance the strength especially after pre-drying at 450°C. Magnesia additions for spinel formation have a detrimental effect on strength regardless of the pre-drying temperature.
Moisture protection of pre-cast shapes by additional packaging is of benefit and reduces and also retards the loss of strength during storage. It depends upon the specific conditions, and what is practical for the particular application. Pre-cast shapes must never be stored outdoors without proper protection.
Previous studies are confirmed, that the loss of strength after storage is reversible when the pieces are dried at the same temperature as before. Therefore the potential loss of strength is important mainly during transportation and installation but less so when used later at higher temperature. The main strength loss appeared after storage for one month. This also supports the results from the studies discussed earlier.
The strength level of the castable used for pre-cast shapes is normally high enough to accommodate the strength loss due to moisture pick up from humidity in the industrial process.
The pure Alphabond binder paste showed abnormal weight increase behaviour during storage, which was higher after a short storage time but was reduced after longer storage times. The reason for this is still unclear and needs to be investigated in further studies.

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