THREE DECADES OF ALPHABOND 300: AN OVERVIEW OF ITS TECHNICAL ADVANTAGES

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ABSTRACT

Alphabond 300 has been used in many applications since it was developed 3 decades ago. In this paper an overview is presented of the different technical advantages for applications where Alphabond 300 is used. Alphabond 300 is a calcia-free hydratable alumina based on pure alumina. In castables containing components such as silica and magnesia the melting temperatures could be reduced when calcia is present in the binding system. Therefore better refractory properties could be achieved with Alphabond 300. The specific surface area of Alphabond 300 is up to 300 m^2/g and therefore the right castable formulations need to be selected having good water demand and rheological behaviour. In general the cured strength is lower in castables with Alphabond 300 compared to those using Calcium Aluminate Cement. In addition to using Alphabond 300 as binder it is also used to improve the properties of cement based castables. Flow and setting properties are more robust when small amounts of Alphabond 300 are added to cement based castables. This is especially true when silica fume of fluctuating quality is used. More reliable castable performance can be achieved with an addition of Alphabond 300.

INTRODUCTION

Alphabond 300 was developed in the 1990s as a hydratable alumina binder. [1] Since then it has been used in several applications to improve the refractoriness of castables in the side wall and bottom of steel ladles, delta sections of electric arc furnaces or ladle furnaces, and in precast refractory shapes. [2-3] To obtain the right performance of refractory castables a selection of the right components has to be made. Castables may contain components with different metal oxides, most individual metal oxides such as alumina, silica, calcia or magnesia have high melting temperatures. When sintering occurs at higher temperatures these components will convert to the most thermodynamically stable phases. In most cases the phases formed will have lower melting temperatures than the original components and the refractoriness of the final material could be lower. In castables with alumina, magnesia, silica and calcia the lowest melting temperature could be increased significantly by leaving out calcia. This can be achieved by replacing Calcium Aluminate Cement as the binder with hydratable alumina. Alphabond 300 is an amorphous alumina with a high specific surface area of around 300 m^2/g. [4] This makes the alumina soluble and alumina hydrates are formed which will lead to strength development. The first types of Alphabond, Alphabond 100 and Alphabond 200, were developed with additives to obtain good rheological properties. In the 2000s Alphabond was further developed and improved and Aphabond 300 was introduced to the market. Alphabond 300 is free of additives. Following Alphabond 300 another additive containing Alphabond, Alphabond 500, was introduced. [5] However, this did not succeed in the market because the additive-free version is preferred by customers because of its higher flexibility in castable formulation. The dispersion and setting can be controlled with the accelerating and retarding dispersing aluminas or with other standard additives systems used in refractory castables. [6]

In addition to using Alphabond 300 individually as a binder it may also be used in combination with cement. Additions of Alphabond 300 to cement containing castables will cause interaction between the binders. [7] During the hydration of calcium aluminate cement, calcium and aluminium ions are dissolved into the pore solution and hydrates based on the hydroxides of calcium and aluminium are precipitated. Alphabond 300 provides additional aluminium ions in the pore solution which influences setting and flow properties of the cement hydration.

In this paper a compilation of research on the technical advantages of Alphabond 300 are reported.

Hydration behaviour of pure Alphabond 300

Alphabond 300 is very hygroscopic and starts to hydrate immediately when it comes into contact with water as shown in figure 1. Here a mix containing 50 weight% Alphabond and 50% water was investigated. The temperature of the mixture rises immediately when Alphabond 300 is mixed with water and in about an hour the temperature is higher than 50°C.

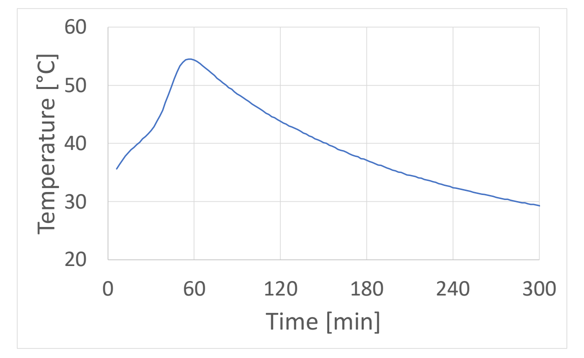

Fig. 1: Exothermal measurement hydration Alphabond 300 with water (1:1)

Heat flow calorimetry and in-situ XRD were performed to determine the hydration mechanism of Alphabond 300. The overlay of the results from both measurements are plotted in figure 2. 3 different heat flow events could be determined. The first peak is a sharp intense peak which is related to the interaction of the amorphous alumina with water. During the first heat flow event no hydrates are formed and therefore workability during this period could be expected. After 4 hours the first hydrate formed is Boehmite which is correlated to the second heat flow event. After 16 hours the third heat flow event occurs which is related to the formation of Bayerite. The formation of hydrates is slower for Alphabond 300 than with calcium aluminate cement. [8] With the slower formation of hydrates slower strength development can also be expected.

Alphabond as binder in castables

The properties of an Alphabond 500 (3wt%) based castable (NCC) were compared to an ultra-low cement (2.5wt%) based castable (ULCC) by Kockegey-Lorenz. [4] As Alphabond 500 behaved like Alphabond 300 with dispersing aluminas ADS/W, the results are also representative for Alphabond 300. The castables were based on alumina, spinel, magnesia and silica fume. Similar hardening times and flow behaviour could be achieved by using 0.5 wt% ADS 3 and

0.5wt% ADW 1 for the ULCC compared to the NCC based on Alphabond 500 which contained additives. It has to be noticed that the wet-out time of Alphabond 500 is clearly higher than cement based castables.

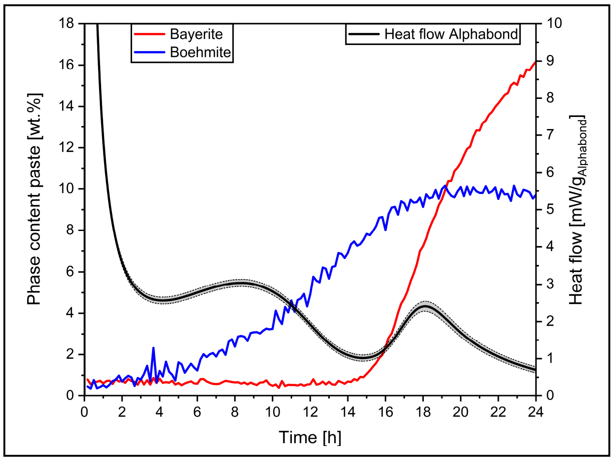

Fig. 2: Heat flow calorimetry of Alphabond (black line) and phase development by in-situ XRD of Boehmite (blue line) and Bayerite (red line)

The 24 hours curing strength of the NCC is higher than that of the ULCC. For a cement based castable the strength could be increased by increasing the cement content, as shown in figure 3. When Alphabond 300 is used as a binder, it's content cannot easily be increased due to the high specific surface area of Alphabond 300. With a higher Alphabond 300 content the water demand will be increased which negatively impacts the strength properties. Therefore a binder content of 3wt% is recommended when using Alphabond 300. The strength levels are increased when the cured bars were dried at 110°C for another 24 hours. The strength levels of the NCC and ULCC are similar. The strength of the NCC is lower after dehydration at 1000°C, while the strength of the ULCC increases at 1000°C. When the bars were further sintered at 1500°C high sintering strength was obtained for the CAC containing castable and for the Alphabond 500 containing castable. The strength is measured when the bars were cooled to room temperature. The liquid phases which were present in the calcia containing castable were crystallized or solidified as amorphous glass phase and didn't affect the strength at low temperature.

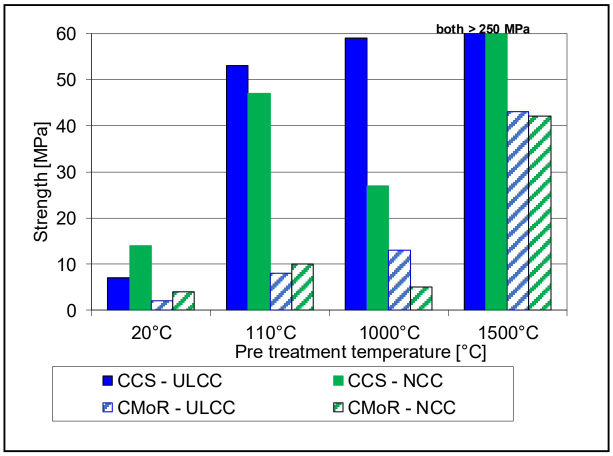

Fig. 3: Strength development of different temperature treatments of NCC and ULCC

The lowest melting temperature of the material will determine the refractoriness of a material. When the material is exposed to high temperatures and pressure the material starts to deform when a melt is formed. The occurrence of melt and its formation temperature in a castable can be determined by refractoriness under load. The dimension change during heating is measured and shown in figure 4. When there is no melt present the materials expand with increasing temperature. Even with small amounts of molten phase, the material starts to contract as the liquid phase acts like a lubricant in the refractories. The deformation occurs at lower temperatures and is more pronounced in the calcia containing castable then in the NCC, due to the low cement content in an ULCC, where the calcia level was only 0.7%. It is expected that a castable with higher calcia content such as a LCC, will form more melt which will impact the refractoriness under load even more.

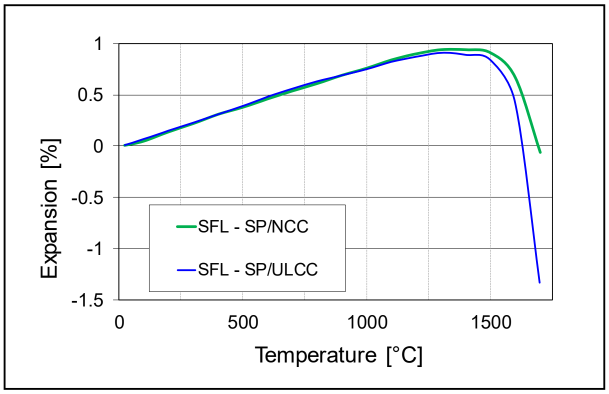

Fig. 4: Refractoriness under load of Calcium Aluminate Cement based castable (ULCC) and Alphabond 500 based castable (NCC)

Drying tests were performed with cubes (40 * 40 * 40 mm) from a self-flowing castable based on CAC and Alphabond. [4] The weight loss was measured as a function of temperature and the drying curves are plotted in Figure 5. The cubes were cured for 24 hours then dried with a heating rate of 1 °C/min while hanging in a furnace equipped with a mass balance. The weight loss of the NCC occurs at lower temperatures than the LCC. This means that when Alphabond is used lower temperatures are sufficient to dry the castables.

During the development of Alphabond there were concerns that castables based on Alphabond 300 would be more susceptible to explosive spalling, due to the formation of aluminium hydroxide gels. Although Alphabond 300 has been used in the refractory industry for three decades there are no major issues reported relating to explosive spalling. The lack of reports on explosive spalling with Alphabond 300 based castables is in line with the results from this drying test.

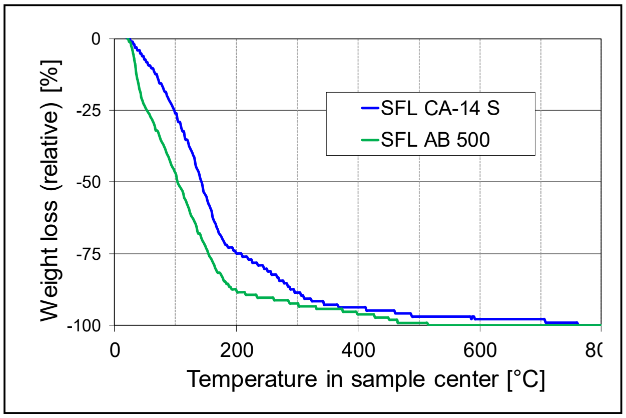

Fig. 5: Water loss over time of Calcium Aluminate Cement bonded castable compared to Alphabond 500 bonded castable

Interaction of Alphabond 300 with cement

Model experiments were performed to understand the interaction between Alphabond 300 and CAC. Heat flow calorimetry was performed with pastes of 50wt% fine tabular alumina (-45 microns) and 50wt% binder. The binder was a mixture of CA-14 S and Alphabond 300 with mixing ratios of, 50/0, 40/10, 25/25, 10/40, 0/50. The results are shown in figure 6.

As described above the formation of hydrates from Alphabond 300 is slow. When a 10wt% of CA-14 S is used with 40wt% Alphabond 300, the formation of the hydrates is accelerated. The formation of heat in the first hours is similar to that with pure Alphabond 300. Almost instantly, when the first hydrates start to form, a sharp heat of hydration peak is observed. This indicates that the strength development could be increased by adding small amounts of CAC. The dormant period of CAC is much longer compared to Alphabond 300. The setting time of CAC is accelerated when 10wt% Alphabond 300 is added to 40wt% CAC and could be even further accelerated by using a ratio with more Alphabond 300.

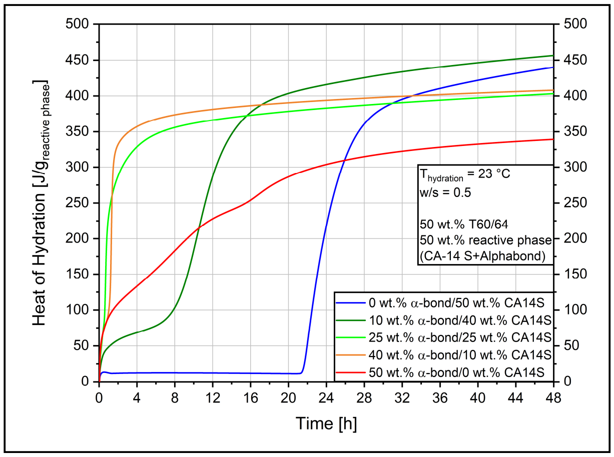

Fig. 6: Cumulative heat flow calorimetry curves of mixtures of Alphabond 300 and CA-14 S as binder

Addition of Alphabond 300 to a cement based castable

Alphabond 300 was used as an accelerator for a silica fume based LCC which is shown in table 1. 1wt% Alphabond 300 and 4wt% of CAC was used instead of 5wt% CAC. To achieve comparable workability and hydration times no accelerator (M-ADW 1) was used and instead of M-ADS 1, M-ADS 3 is needed to retard the hydration. With the same amount of water higher flow values were achieved.

Tab. 1: Recipe of silica fume based LCC

		LCC-CAC/AB-300	LCC-CAC
Tabular T60/T64		77	77
Raw Kyanite		5	5
Reactive alumina		10	10
Silica fume		3	3
Binder	AB-300	1	
	CA-14 M	4	5
Additives	M-ADS 1		0.7
	M-ADS 3	1	
	M-ADW 1		0.3
Water		4.5	4.5
Self Flow	10 min	258	205
	30 min	248	223
	60 min	184	202
EXO	Start 1	77` / 24.6°C	65` / 24.3°C
	Start 2	4.2 h / 27.1°C	3.4 h / 26.3°C
	Max	5.8 h / 30.8°C	5.4 h / 28.8°C

A higher cured strength was obtained when Alphabond 300 was added, as shown in figure 7. This could be explained by the faster setting behaviour. The dried and fired strength levels from the castables of both binder systems are similar. The main advantage of addition of Alphabond 300 could be seen in the setting and flow behaviour of the castable.

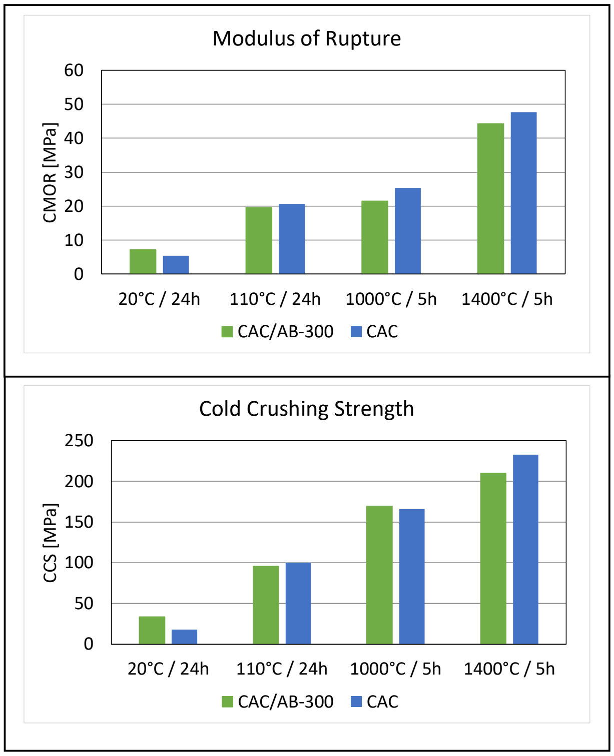

Fig. 7: Strength development of different temperature treatments of NCC and ULCC. Cold Modulus of Rupture (top) and Cold Crush Strength (bottom)

It is well known that different qualities of silica fume could negatively impact the flow behaviour especially with regard to early flow decay. [9] Alphabond 300 improves the flow behaviour of the castables. Therefore different grades of silica fume were used in the LCC. As expected different flow properties were found as can be seen in figures 8a and b. For 2 grades of silica fume the standard castable ceased flowing after 30 minutes. Alphabond 300 counteracts against fluctuations with different silica fume grades. All silica fume grades still had good flow properties after 30 minutes when Alphabond 300 was added.

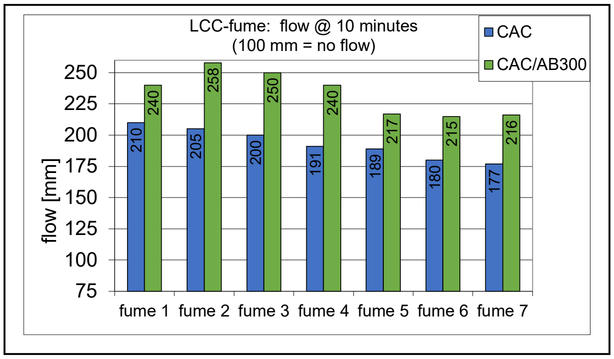

Fig. 8a: Flow values after 10 minutes of LCC with different qualities silica fume

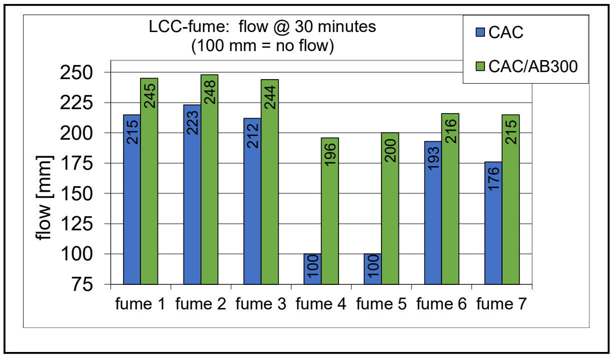

Fig. 8b: Flow values after 30 minutes of LCC with different qualities silica fume

Addition of calcium aluminate cement to an Alphabond 300 based castable

In the model system with CAC and Alphabond 300 it is found that a relative small amount of CAC will accelerate the hydrate formation and with that it is expected that the strength development will also be accelerated. To determine the impact on strength small amounts of CAC were added to alumina-spinel based NCC castables. The castable recipe used is shown in table 2. The calcia content is increased slightly when 0.25wt% or 0.5wt% CAC is added to the castable and the impact on the refractoriness is expected to be limited.

Tab. 2: Recipe for NCC with CAC additions

		NCC	NCC	NCC
Tabular		80	80	80
E-SY 2000		15	15	15
Reactive Al_2O_3		1.5	1.5	1.5
Silica fume		0.5	0.5	0.5
Binder	AB-300	3	3	3
Additives	ADS 3	0.8	0.8	0.8
	ADW 1	0.2	0.2	0.2
Water		4	4	4
CA-14 M		0	0.25	0.5

As shown in figure 9, with an addition of 0.25wt% CAC the cured strength increases from a modulus of rupture of 1.6 MPa to 4.2 MPa and the cold crushing strength increases from 12.4 MPa to 18.6 MPa. The strength could be increased even more when more CAC is added. A modulus of rupture of 5.6 MPa and a cold crushing strength of 22.2 MPa were obtained when 0.5wt% CAC was added.

The strength after firing the bars at 1000°C is also significantly improved with the addition of CAC. The modulus of rupture could be increased from 7.8 MPa to 17.1 MPa and 18.3 MPa with additions of respectively 0.25wt% CAC and 0.5wt% CAC. The cold crushing strength could be increased from 60.5 MPa to 86.6 MPa and 101.0 MPa with additions of respectively 0.25wt% CAC and 0.5wt% CAC. It is clear that the accelerating effect of CAC on the hydrate formation of Alphabond 300 is having a positive effect on the final strength. The effect of the higher strength is even present after complete dehydration when the test bars were exposed to 1000°C.

CONCLUSIONS

Alphabond 300 could be used to replace calcium aluminate cement as a binder when calcia lowers the melting temperature in castables containing alumina, magnesia and silica. Castables based on Alphabond 300 have improved hot-properties over cement based castables. The cured and dried strengths of castables based on Alphabond 300 is lower. It was found that if higher cured and dried strength is needed small amounts of CAC may be added to increase the strength significantly.

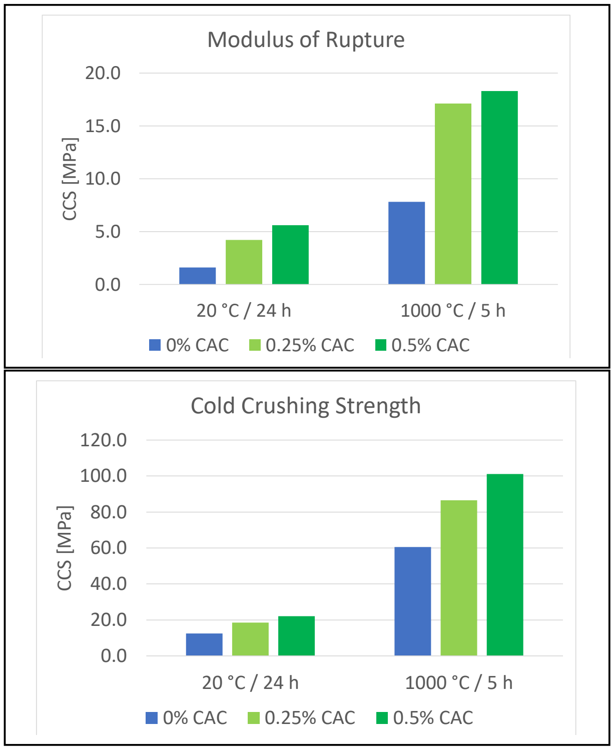

Fig. 9: Strength development of different temperature treatments of NCC and ULCC. Cold Modulus of Rupture (top) and Cold Crush Strength (bottom)

Alphabond 300 could also be added to CAC based castables which has an accelerating effect. The addition of Alphabond 300 also improves the flow behaviour and Alphabond 300 is counteracting against flow decaying impurities from within silica fume.

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