IMPROVEMENTS IN WORKABILITY BEHAVIOR OF CALCIA-FREE HYDRATABLE ALUMINA BINDERS

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SUMMARY

Alphabond is a hydratable alumina used as a binder in no-cement castables, e.g. for steel ladle and other applications. Introduced in the 1990's, the market interest in this calcia free hydraulic binder has considerably increased over the last few years. Although the original Alphabond behaved in a similar manner to high purity calcium aluminate cement based castables with respect to working time, setting time, water demand and flow properties, it had some unique characteristics that required special attention during application. Generally, dense castables using Alphabond have required extended mixing time to fully "wet out". A new and improved Alphabond binder is presented here, which significantly reduces the mixing differences as compared to cement bonded castables. It reduces the required mixing time to fully "wet out" to about 120 seconds, a level that is comparable to usual low cement castables. The different drying behaviour of Alphabond castables compared to cement castables has been investigated. The advantages in hot properties of calcia free Alphabond spinel forming castables are discussed.

INTRODUCTION

Numerous publications and papers [1-9] in recent years demonstrate the increasing interest and applications of calcia free high performance castables using hydratable alumina binders as an advanced alternative to calcium aluminate cements. The main advantages over low cement (LC) or ultra low cement (ULC) castables are described as improved slag resistance and hot properties, as well as superior performance in applications which cannot tolerate any CaO content in special refractory linings. Drawbacks in using hydratable alumina binders are known to include the need for longer mixing times until wet out is achieved, along with the risk to add more mixing water than recommended. This circumstance led to the use of hydratable alumina bonded castables predominantly for the more controllable manufacturing of "in-house" produced pre-cast shapes rather than on-site applications such as castables for monolithic ladle lining. Such on-site installations may require quick mixing of batches or potentially continuous mixing during on-site installations and extended wet-out time can cause production upsets.

This paper describes the newly developed hydratable alumina binder Alphabond 500 which eliminates cumbersome and time consuming mixing processes with regard to wet out time.

TYPICAL DATA OF ALPHABOND 300 AND THE NEW ALPHABOND 500

The chemical composition and particle size distribution of Alphabond 300 and 500 are listed in **Table 1**. The new grade Alphabond 500 shows a higher loss on ignition (LOI) compared to Alphabond 300 and a modified particle size distribution.

Tab. 1: Alphabond 300 and Alphabond 500 (contains additives), typical product data

	Alphabond 300	Alphabond 500
Chemical Composition [wt.-%]		
Al_2O_3*	91	84
CaO	< 0.1	0.6
Na_2O	0.2	0.3
SiO_2	< 0.1	0.3
MOI (%loss 25-250°C)	2.9	6.0
LOI (%loss 250-1000°C)	6.0	9.2
Particle Size Distribution		
d50 [µm]**	2.3	5.2
d90 [µm]**	5.1	14.2
d50 [µm]***	3.6	6.3
d90 [µm]***	8.0	17.9

*) Al_2O_3 by difference = [100%-(sum of impurities-MOI-LOI)]
**) Sedigraph 5100
***) Microtrac VSR

The higher LOI of Alphabond 500 results from high performance additives for dispersion and set control incorporated in the product using a proprietary co-formulating process. The modified particle size distribution contributes to further improvement in wet out time. **Table 1** provides data for Alphabond measured by both Sedigraph 5100 and Microtrac VSR. Differences in d50 and d90 for identical samples are a result of differences in the principles of the two methods, by either sedimentation or laser beam diffraction as well as the corresponding algorithms of particular instrument software set up. Even though Microtrac VSR reports a coarser particle size distribution compared to Sedigraph 5100, the laser granulometer Microtrac VSR will be the preferred instrument for use in quality assurance as it provides precise and reproducible results within a shorter time. **Figure 1** compares the particle size distribution of Alphabond 300 and Alphabond 500 by relative weight-% as measured by Mictrotrac VSR. The new Alphabond 500 has a lower proportion of fines, however the top size is comparable to Alphabond 300. The particle size distribution of the described additive free Alphabond 300 product will also be modified towards the range of the new additive containing Alphabond 500.

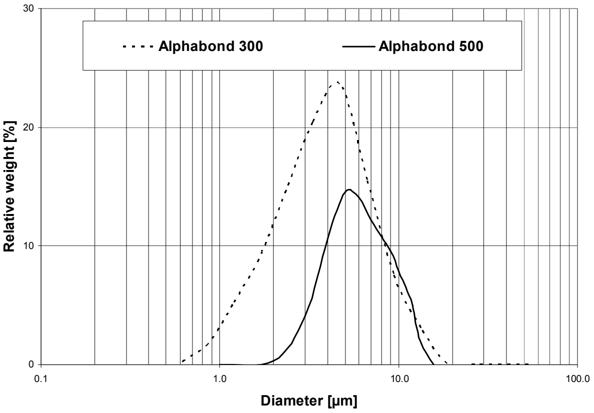

Fig.1: Particle size distribution of Alphabond 300 and Alphabond 500 by Microtrac VSR

DEFINITION AND DETERMINATION OF WET OUT TIME

The wet out time is the time after water addition until a refractory castable becomes homogeneously wet after water addition. The typical sequences during the mixing process are:

- Dust and fine fraction disappear
- The coarse fraction becomes visible
- Reduction of noise, depending on mix and mixer design
- Dry pellets at about 8 mm diameter are formed
- Pellets form clusters or lumps and get a shiny surface

The mix is homogeneously wetted when the surface of the lumps become shiny, hence the end point for the so called wet out time is reached.

Figure 2 shows a castable in a commonly used laboratory mixer at the point of wet out time determination.

Fig. 2: Castable wet out time end point in a laboratory mixer

MIXING BEHAVIOUR USING ALPHABOND 300 AND 500

The experimental self flowing castables SFL AB 300 and SFL AB 500 have been formulated to compare Alphabond 300 with Alphabond 500. Raw materials, formulation, self flow behaviour, wet out times and physical data are listed in **Table 2**. All test mixes were prepared in batches of 5 kg dry constituents at 20°C room temperature using a planetary mixer type Hobart A 200 at velocity stage 1, giving a rotational speed of the paddle of 50 rpm.

As the new Alphabond 500 incorporates dispersing and set control additives, additional additives are not needed as long as the proportion of Alphabond 500 is 3% or more.

The determination of self flow used the methods comprehensively described by Kriechbaum, et al. [10]. Dimensions of the self flow test cone are 100 mm lower diameter, 70 mm upper diameter and 80 mm height.

Comparable self flow values were achieved using high performance dispersing alumina in a selected admixture of ADS 3 and ADW 1 for the mix containing Alphabond 300.

The wet out time was determined according to the method described above. The use of Alphabond 500 shows a remarkable improvement of wet out times of approximately 50% of Alphabond 300. Wet out times were 100 to 140 seconds with Alphabond 500. This range is similar to that for advanced LC- or ULC- castables which is typically 80 to 120 seconds under these test conditions.

The EXO max., which gives the time of the highest temperature rise during setting only indicated a small peak after more than 30 hours which is typical for castables using a hydratable binder earlier described by Vance and Moody [1]. However, the setting of

Castable Component	**SFL AB 300**	**SFL AB 500**
T-60/T-64 up to 6 mm [%]	70	70
0-0.045 mm LI	10	10
0-0,020 mm	7	7
Reactive Alumina CTC 30 [%]	10	10
Binder Alphabond 300 [%]	3	-
Binder Alphabond 500 [%]	-	3
Sum (%)	100	100
Dispersing Alumina ADS 3 [%]	0.75	-
Dispersing Alumina ADW 1 [%]	0.25	-
Mixing water [%]	4.5	4.5
Wet Out Test [s]	**270-310**	**100-140**
Self Flow [mm]		
10 min	230	230
30 min	225	220
60 min	220	185
Hardening time [h]	3	3
Physical data		
CMOR [MPa]		
20°C/24h	1	1
110°C/24h	13	12
1000°C/5h	2	3
1500°C/5h	39	36
CCS [MPa]		
20°C/24h	7	8
110°C/24h	60	69
1000°C/5h	7	9
1500°C/5h	147	121
Bulk density [g/cm³]		
110°C/24h	3.12	3.11
1000°C/5h	3.08	3.07
1500°C/5h	3.06	3.13
PLC [%]		
110°C/24h	±0	-0.03
1000°C/5h	-0.1	-0.02
1500°C/5h	-0.5	-0.5

Tab. 2: Composition and properties of self flowing test castables with Alphabond 300 and Alphabond 500

Alphabond castables cannot be appropriately measured by this method and was therefore discarded. The mixes hardened after 3 hours at 20°C room temperature, which was checked by hand test.

A more advanced ultrasonic method to characterize the setting behaviour of hydratable alumina bonded castables is discussed in detail by Cölle, et al. [9]. An electronic device detects the changing propagation velocity over time of an ultrasonic pulse, corresponding to the castables hardening kinetics. Cölle et al. observed a remarkably lower dependency of the setting times on temperature with Alphabond castables compared to low cement castables. Whereas for the low cement castable the setting start increased from about 135 minutes at 25 °C to about 730 minutes at 5 °C, the Alphabond castable shows no difference in setting start between 25, 20 and 15 °C (about 40 minutes), and only at 5 °C did the setting start increase to about 90 minutes. This robustness of Alphabond mixes with regard to the setting behaviour at lower temperatures is a significant advantage for on-site applications, where conditions cannot always be as well controlled as for pre-cast shape production.

Both the bulk density and the mechanical strength of the test mixes are at the same level for the Alphabond 300 and Alphabond 500 test mix (**Table 2**). Also the permanent linear change at 1500 °C is the same.

DRY-OUT BEHAVIOUR OF ALPHABOND CASTABLES

Vance and Moody [1] advised extreme caution during castable dry-out using hydratable alumina binders due to possible explosive spalling.

For a comparison between dry-out behaviour of hydratable alumina binder and cement bonded castable, the mix SFL AB 500 was modified to SFL CA-14/5 with 5% CA-14 S, a 70% Al_2O_3 calcium aluminate cement instead. The same mixing water addition of 4.5% was used along with 1% dispersing alumina addition, consisting of 0.75% ADS 3 and 0.25% ADW 1. The 10% proportion of tabular alumina T-60/T-64, size 0-0.045 mm in SFL AB 500 was reduced to 8% in order to maintain a comparable particle size distribution.

For the investigation of dry-out behaviour, the following test was carried out at DIFK / Bonn, Germany: Small cubes (40x40x40 mm) were cast with a thermocouple wire ending in the centre of the cubes. After curing 24h at room temperature the cubes were placed in a special designed furnace using a carrier plate and being connected to an external balance. The furnace was heated up at 1°C/min, which is normally considered an adequate drying speed for monolithic linings at this thickness. The loss of weight was continuously measured at rising temperatures.

Figure 3 depicts dry-out recorded from room temperature up to 800°C for the low cement and Alphabond castable. The total weight loss is standardized to 100%. It clearly demonstrates that dry-out of the Alphabond containing mix has different characteristics as compared to a cement bonded system. It is apparent that special attention is required for hydratable alumina castables at lower temperatures. While the Alphabond castable loses 50% of its initial moisture by 100°C, the LCC is only at 30% loss. At 200°C the Alphabond castable is near complete dry-out at 90% whereas the LCC is still at 75% weight loss. It is this rapid moisture loss combined with the low permeability of hydratable alumina castables that resulted in the explosive spalling failures in the early days of their use. However, a great deal of drying and firing experience has been gained in the past years and adequate equipment is now available to cope with the special drying requirements of hydraulic bonded monolithic shapes and linings [11, 12].

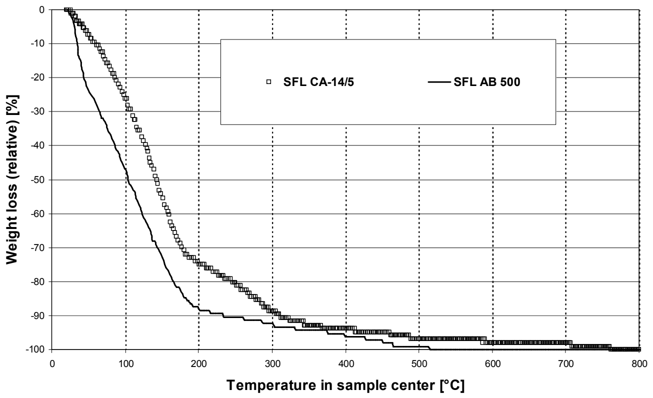

Fig. 3: Dry-out over temperature comparing calcium aluminate cement bonded castable with Alphabond 500 castable

HOT PROPERTIES OF ALPHABOND 500 SPINEL FORMING CASTABLE

Applications to date using hydratable alumina binders are predominantly for pre-cast shape manufacturing. As the newly developed Alphabond 500 shows significant improvements in wet out behaviour and therefore mixing times, it has potential for on-site installations.

An interesting on-site monolithic ladle lining option follows the trend to use alumina magnesia spinel/spinel forming castables for improved slag resistance and hot properties.

The test castables SFL SP/CAC and SFL SP/AB were selected to compare physical properties with special attention to the hot properties in a cement bonded and cement free system.

Table 3 shows the mix formulation. Both concepts use tabular alumina T-60/T-64 for the coarse fraction, alumina rich spinel AR 78 in the fines up to 0.5 mm size, calcined and reactive alumina, fine MgO and silica fume. The mix SFL SP/CAC uses 2.5% CA-14 S calcium aluminate cement as an ULC castable concept with a 1% dispersing alumina addition, whereas SFL SP/AB has 3% Alphabond 500 with its incorporated additives. Mixing water is 5% in both cases. The mixes hardened after 2.5 hours at 20°C room temperature.

Both castables show comparable results for cold modulus of rupture (CMOR), cold crushing strength

Castable / Component	**SFL SP/CAC**	**SFL SP/AB**
T-60/T-64 up to 6 mm [%]	50	50
Calcined and reactive alumina [%]	25	24.5
Spinel AR 78 up to 0,5 mm [%]	20	20
MgO fines [%]	2.0	2.0
Silica fume [%]	0.5	0.5
Cement CA-14 S [%]	2.5	-
Alphabond 500 [%]	-	3.0
Sum (%)	100	100
Mixing water [%]	5.0	5.0
Dispersing Alumina ADS 3 [%]	0.5	-
Dispersing Alumina ADW 1 [%]	0.5	-
Self Flow [mm]		
10 min	230	230
30 min	225	220
60 min	220	185
Hardening time [h]	2.5	2.5
Physical data		
CMOR [MPa]		
20°C/24h	2	4
110°C/24h	8	10
1000°C/5h	13	5
1500°C/5h	43	42
CCS [MPa]		
20°C/24h	7	14
110°C/24h	53	47
1000°C/5h	59	27
1500°C/5h	260	265
Bulk density [g/cm³]		
110°C/24h	3.04	3.03
1000°C/5h	3.00	3.01
1500°C/5h	3.04	3.06
Apparent porosity [%]		
110°C/24h	15.9	11.1
1000°C/5h	17.7	18.5
1500°C/5h	16.5	17.4
Chemical analysis of test mixes [wt.-%]		
Al_2O_3	92.4	93.1
MgO	6.4	6.4
SiO_2	0.5	0.5
CaO	0.7	-
Hot properties (all specimens prefired at 1500°C/5h)		
HMOR [MPa]	2	2
RUL data (load:0.2 MPa)		
D max. [% @ °C]	0.91 @ 1300	0.95 @ 1350
T 0.5 [°C]	1602	1640
T 1 [°C]	1645	1700

Tab. 3: Chemical composition and properties of alumina magnesia spinel self flowing ultra-low cement and Alphabond 500 castable

(CCS), bulk density and apparent porosity when prefired at 1500°C/5h. At lower temperatures, typical differences appear between cement bonding and use of hydratable alumina binder. Especially at 1000°C/5h pre-firing , the Alphabond castable shows a more pronounced drop in strength which is typical for castables using hydratable alumina binders since the ceramic bonding does not begin until ~1000°C. However, an acceptable strength level is reached. The Alphabond castable also shows a reduced apparent porosity at 110°C as a result of the aluminium hydroxide gel formations previously reported by Vance and Moody [1].

Alumina-magnesia spinel forming castables typically include small silica fume additions for expansion control to cope with the volume increase of the spinel formation from the reaction of Al_2O_3 and MgO. Therefore, LC or ULC spinel forming castables contain Al_2O_3, MgO, CaO and SiO_2 as chemical components.

The melting behaviour of such compositions has been evaluated by means of the quaternary CaO-MgO-Al_2O_3-SiO_2 phase diagram [13, 14]. The theoretical onset of melting at the given chemical composition of SFL SP/CAC is below 1390°C whereas SFL SP/AB is almost 200°C higher at 1578°C. This difference should reflect in increased hot strength for the cement / CaO-free spinel forming castable.

The hot modulus of rupture (HMOR) and refractoriness under load (RUL) are determined at DIFK/Bonn on specimens prefired at 1500°C/5h. Testing procedures are in compliance with DIN EN 993-7 for HMOR and DIN EN 993-8 for RUL measurements. SFL SP/CAC and SFL SP/AB show equal hot modulus of rupture at 2 MPa as average result of 5 individual measurements.

However, refractoriness under load shows significant differences (see **Figure 4**). The creep resistance of the Alphabond castable is higher compared to the ULC castable. T 0.5 is 40°C higher and T 1 is 55°C higher compared to the cement containing castable; T 1 of the Alphabond castable reached 1700°C at the end of temperature recording and test.

Since SFL SP/CAC follows an ULC castable concept with 0.7% CaO, it can be expected that frequently used LC castable formulations at a typical level of 5% content of calcium aluminate cement, with a total CaO at ~1.5%, probably would show an even more pronounced difference in refractoriness under load.

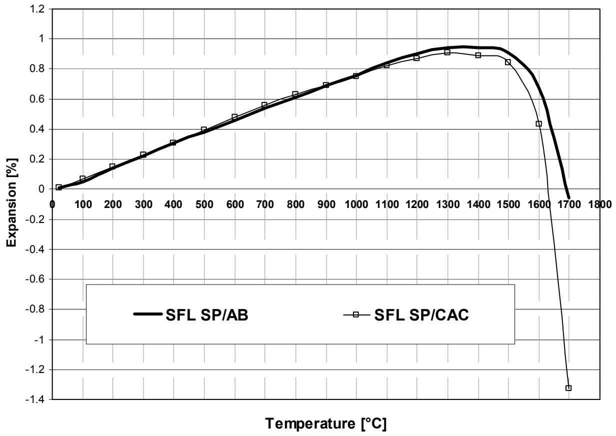

Fig. 4: Refractoriness under load (0.2 MPa) of alumina magnesia spinel self flowing ultra-low cement castable and Alphabond 500 castable

CONCLUSION

The newly developed hydratable alumina binder Alphabond 500 clearly demonstrates a quantum leap improvement in wet out time by reaching workability in times previously only achieved by cement bonded castables. As demonstrated by the test castables, the flow and set behaviour is comparable to that for the established Alphabond 300 product. Therefore to cope with their demanding mixing and placing requirements, Alphabond 500 is expected to quickly become the product of choice in castables for on-site casting.

Alphabond as calcia free hydratable alumina binder offers the advantage of robust setting behaviour with regard to temperature and improved hot properties, especially for silica containing spinel forming castables. This offers the refractory engineer new opportunities for an advanced generation of castable developments for monolithic steel ladle lining.

The drying of Alphabond castables requires special attention because of the inherent de-hydration behaviour of hydratable alumina. The water is released in a more narrow temperature range compared to cement bonded castables.

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