Alcoa Industrial Chemicals

Steelplant Refractories Containing Alphabond Hydratable Alumina Binders

by
M. W. Vance and K. J. Moody
Alcoa Industrial Chemicals, Pittsburgh, PA

October 1996

TECHNICAL BULLETIN

Alcoa Technical Bulletin

Steelplant Refractories Containing Alphabond Hydratable Alumina Binders

by

M. W. Vance and K. J. Moody
Alcoa Industrial Chemicals, Pittsburgh, PA

ABSTRACT

Potential benefits of eliminating calcia from a low cement castable composition in order to develop superior properties are improved hot strength, thermal shock resistance, resistance to corrosion by steel making slags, and decrease in potential reducible oxides that could lead to contamination of steel. This paper explores practical information concerning implementing calcia-free no-cement castables containing Alcoa's Alphabond® hydratable alumina binder. For example, parameters associated with mixing, casting, and successful dewatering precast shapes are described. Specific examples are given of processing data and experience that may be applied to fabricating refractory shapes.

This paper also describes the opportunities gained by using Alphabond as an alumina source to develop in situ bonding in calcia-free no-cement castables to form mullite and magnesium aluminate spinels.

No-cement castables containing hydratable alumina binders are now being used extensively in the following components associated with steel making equipment: electric furnace delta sections, metal treatment lances, continuous caster dams, weirs and impact pads, and ladle impact pads and well blocks. They may also be used in field cast monolithic linings where firing is carefully controlled.

Contents

Introduction

Calcium-free hydratable alumina binders (HABs) are increasingly used in no-cement refractory castable compositions associated with unique applications where the performance of the matrix is critical to application performance. For example: An inert matrix containing Alcoa's **Alphabond®** binders can provide a non-reactive protective border surrounding aggregates for controlling slag resistance, fracture toughness, residual hot strength after thermal cycling and erosion resistance. Alphabond constitutes a new family of binders and are gaining wide acceptance for use in no-cement castables that contain <0.1% CaO.[1] The advantage is that Alphabond binders reduce the formation of calcium aluminosilicates that may provide high temperature bonds when exposed to steelmaking temperature.

Table I. Characteristics of Alphabond Hydratable Alumina Binder (HAB and HAB/S) Materials

Characteristic	Alphabond 100	Alphabond 200
Chemical Analysis, %		
Al_2O_3 by difference (as-received)	90	90
CaO (calcined basis)	<0.1	<0.1
SiO_2 (calcined basis)	<0.1	<0.1
Na_2O (calcined basis)	0.5	0.5
Others (calcined basis)	0.5	0.5
LOI as-received	6.5	6.5
MOI as received	4.5 max	4.5 max
-325 mesh	100	100
Surface Area (m^2/gm)	271	271
Packed Bulk density (lb./cu.ft.)	33.2	32.6
Particle Size (microns)		
D10	0.6	0.6
D50	2.5	2.5
D90	5.1	5.1
Characteristic	CALTAB 605A	CALTAB 605S
Working Time (minutes)	45	65
Casting Water (%)	5.4	5.4
Strength (psi-N/m2)		
Air Cured (24 hr.)	861-5.9	571-3.9
Dried (110°C/230°F, 24 hr.) 230°F, 24 hr.)	1649-11.2	1016-6.9
Fired (1370,°C/2500,°F, 5 hr.) 2500,°F, 5 hr.)	2603-17.7	4679-31.8
HMOR (1500°C/2732°F, soaked 12 hr.)	500-3.4	900-6.2

Notes: Dated 4/21/95, Revised 10/3/95 and 3/5/96. Source: Alcoa Industrial Chemicals, Vidalia Operations Batching

Alphabond binders are also useful in developing stable bonds for high purity metallurgical processes where Ca and Si pick-up are of concern. The special requirements of castables containing microsilica have necessitated the development of two Alphabond products containing admixtures that adjust working time: One system used in silica-free castables is designated as an "HAB" (or Alphabond 100). The other is generically designated as "HAB/S" (or Alphabond 200).

Specific properties of both Alphabond binders are listed in Table I.[2,3] Surface area and particle size data all indicate that they are finely divided transition alumina particles that readily hydrate and bond with other particles.

One of the key features of Alphabond is that it is capable of being used for casting that requires vibration to place and in self-flow castables. Often, Alphabond products can be substituted for calcium aluminate cements (CACs) in low cement castables without having to extensively modifying the composition.

Recent developments using Alphabond in self flow mixes are described later. Although Alphabond acts similar to 80% CACs with respect to working time, initial and final setting time, water demand, and flow properties, they have some unique characteristics that should be considered for their use in various applications.

Alphabond, unlike CAC, does not require humidity to develop strength but controlled curing is necessary to avoid surface crazing. Air drying an acceptable time under ambient conditions (>18°C, 65°F) is all that is required to develop suitably rigid shapes ready for stripping from molds. Cured strength development as a function of time at ambient temperature is shown in Figure 1. This process may be accelerated by applying some heat (up to 66-93°C, 150-200°F) to enhance strength for demolding.

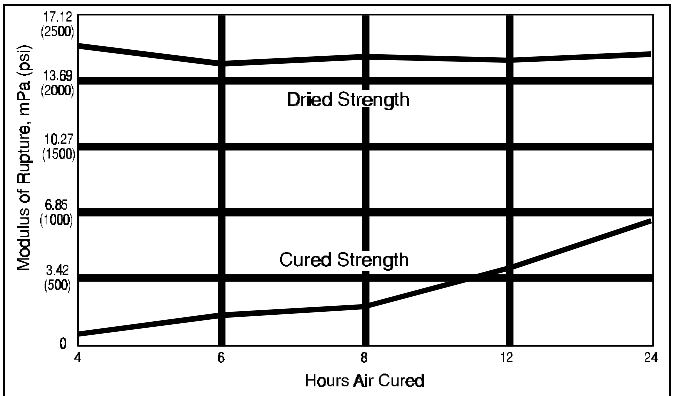


Figure 1. A typical strength development curve for Alphabond HAB at room temperature, 23°C (74°F).

A major goal of this paper is to provide recommendations for firing to ensure crack free parts and minimize explosive spalling when firing precast shapes and *in situ* firing monolithic construction.

Batching

Alphabond is only recommended for use in no-cement castables in lower concentrations from 3 to 7 weight %.[4] Current data shows that the shelf life of an unopened bag is six months using the current packaging. Once Alphabond is exposed to humid environment, bond strength will be rapidly compromised and immediate use is recommended. Small amounts of standard deflocculants may be added to enhance wetting and flow. Lithium carbonate can be added to accelerate setting and strength development. It is recommended that lithium carbonate be added in 0.01% increments based on the mix weight for accelerating set time and advancing strength development. Sodium hexametaphosphate (SHMP) has been effective in enabling good flow properties with most microsilicas and citric acid may be used to effectively reduce water demand. Darvan 7S (sodium polymethacrylate—product of R. T. Vanderbilt Co.) is more effective in achieving good flow for silica-free high alumina matrix materials especially those containing reactive aluminas such as A1000SGD and A3000FL.

Mixing

Generally, dense castables using Alphabond may require additional time to wet out after the water addition is made (1-2 minutes dry mixing followed by 4-5 minutes wet mixing). During mixing, some castables will start to climb and stick to the Hobart mixer bowl just prior to wetting out. Sufficient speed for adequately wetting the mix is required (60 RPM minimum). With some mixers, obtaining adequate mixer speed may be complicated by the addition of stainless steel wire fibers. The general reaction to add more water to accelerate wetting and flow beyond optimum levels for casting and strength should be avoided because of the tremendous impact on density, strength, and slag resistance with corresponding extension of working time that results (see Figures 2 and 3). High intensity mixers (for example, Eirich) are equally effective in developing suitable flow with minimum water content in large batches.

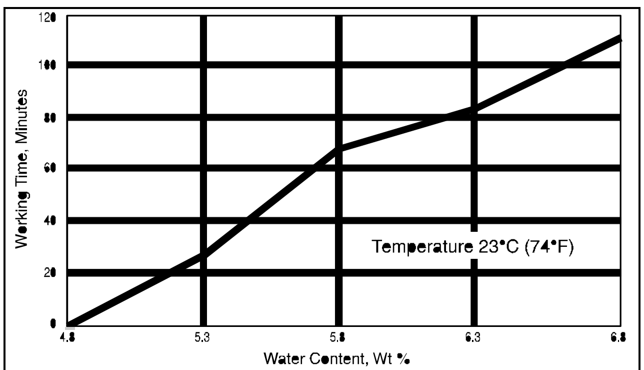


Figure 2. Working time as function of water content

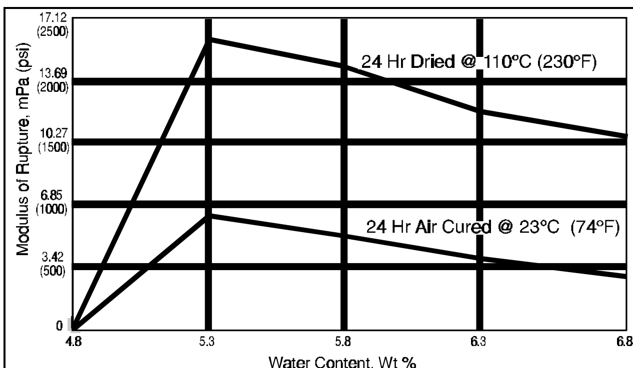
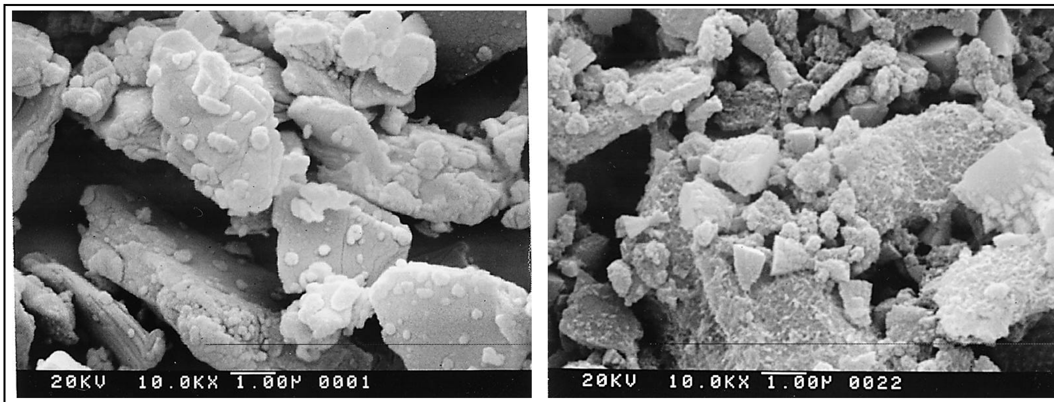


Figure 3. Strength after air curing and drying at increasing water contents. (CALTAB 605A with Alphabond 100)

The ability to form adequate strength depends on the surface hydration of Alphabond 100 particles which is shown in the photomicrographs in Figure 4. Preparation of Alphabond-containing castables at temperatures of less than 18°C (65°F) should be avoided because of retarded strength development. If mixing and casting temperatures fall too low, the hydrated bonds simply do not form rapidly enough to develop adequate strength. During cold weather, warming water and ingredients or locally heating the casting area is recommended. Conversely, temperatures of greater than 38°C (100°F) should be avoided to allow sufficient working time to place the material and to minimize possible flash setting.



As-received *Hydrated*

Figure 4. Alphabond 100 Hydratable Alumina Binder (HAB) particles in the as-received state and after hydration for 24 hours at 22°C (72°F).

[Note: All micrographs have been reduced for printing purposes.]

Casting

For vibratable compositions, working time and batch size should be planned to minimize the possibility of forming lamination folds that would interfere with developing a homogeneous monolithic structure.[5] Vibration levels and times used for vibratable 80% CAC low cement castables that normally exhibit thixotropic casting behavior should be applied to castables containing Alphabond. In dry conditions, if humidity controlled curing capability is not available, parts should be covered with plastic sheeting to avoid crazing or dusting and plastic should be used to cover each layer of large parts between pours to enable knitting. Silica-free and microsilica-containing self flow mixes have been developed that require little or no vibration to place and de-air. As mentioned previously, casting tempreture should be greater that 18°C (65°F).

Setting and Curing

To avoid internal damage, as-cast parts in the mold (especially large castings) should be moved to the furnace for firing before the part has set.[5] Or, when casting is completed, adequate residence time in the mold or form is required to develop suitable strength prior to demolding for firing. An example of strength development in a high alumina/Alphabond 100 composition as a function of temperature exposure is given in Figure 5. The minimum recommended curing temperature is 18°C (65°F). For a particular castable composition, strength will vary according to ambient conditions, size of part, mold design, de-molding practice, and handling the part may experience during loading and unloading the furnace. (Normal rule of thumb is a minimum of 150 psi or about 1 mpa.)

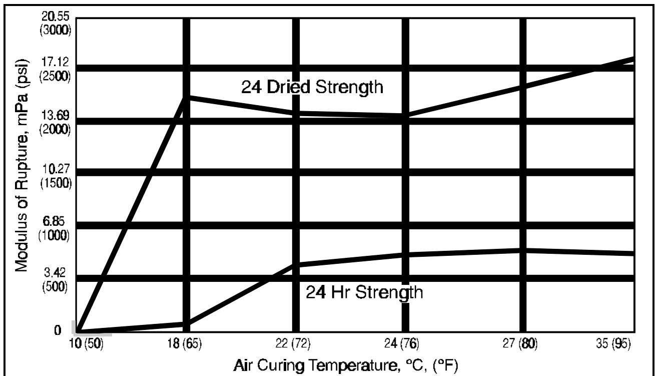


Figure 5. Strength development versus air curing temperature. These CMOR values are for 17.8 x 2.5 x 2.5cm (7 x 1 x 1 in.) bars. (CALTAB 605A with Alphabond 100).

Firing

For optimum strength development and to avoid cracking or explosive spalling, it is essential to understand the dewatering associated with cast parts containing Alphabond.[5] This is best accomplished using thermogravimetric (TGA and TGA') data for neat Alphabond. This data describes the critical points where water vapor releases. Characteristic TGA/TGA' data for a hydrated neat Alphabond 100 paste is shown in Figure 6. The first derivative with respect to time helps show the rates of dewatering as a function of

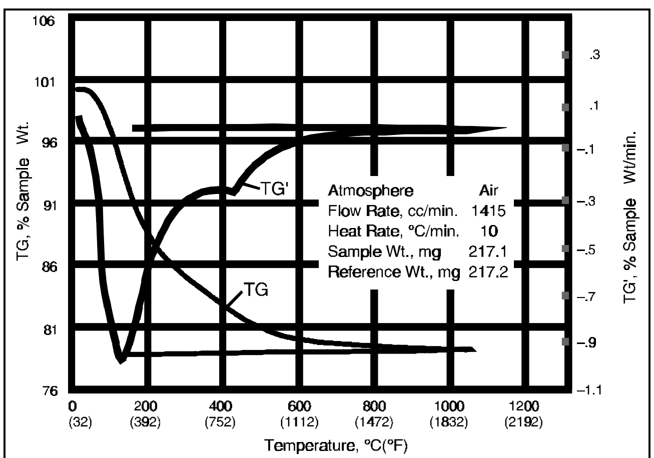


Figure 6. Thermogravimetric analysis of Alphabond 100 HAB (neat) hydrated 24 hours before heating.

increasing temperature. The most rapid weight loss peaks at 140°C (284°F) and dissipates at 300°C (543°F).

Studies on NCCs revealed that mixes containing microsilica have very low permeability values when processed at temperatures less than 18°C (65°F). See Table II.

Table II. Permeability values for a no-cement castable as a function of condition

Mix Temperature	Setting Time	Conditioning Temperature	Permeability (centidarcies)
1.7°C (35°F)	>10 hr.	cured 22°C (72°F), 24 hr.	0.04
		dried 110°C (230°F), 24 hr.	0.00
		fired 232°C (450°F), 2 hr.	0.06
		fired 538°C (1000°F), 2 hr.	0.11
10°C (50°F)	6 hr.	cured 22°C (72°F), 24 hr.	ND
		dried 110°C (230°F), 24 hr.	0.00
		fired 232°C (450°F), 2 hr.	0.08
		fired 538°C (1000°F), 2 hr.	0.08
22°C (72°F)	70-90 min.	cured 22°C (72°F), 24 hr.	0.08
		dried 110°C (230°F), 24 hr.	0.07
		fired 232°C (450°F), 2 hr.	0.20
		fired 538°C (1000°F), 2 hr.	0.16

Note: 2 in. cubes, low moisture castable with Alphabond 200. ASTM C-577-87

These values tend to increase slightly when processing at temperatures greater than 18°C (65°F). Also, some release of steam from mechanical water that remains in pores will contribute to venting difficulties. Applying heat to the part must be performed very carefully at temperatures from 90 to 276°C (194-500°F) to avoid explosive spalling. The rate of loss reaches its maximum at aboiut 150°C (300°F). This is normally the temperature range where castables containing CACs are heated more rapidly. Once the entire part has passed the critical temperature range, the part may then be heated more rapidly at a safe rate. Small amounts of water vapor still evolve at higher temperatures from 276°C (500°F) up to 665°C (1200°F) but these emissions have not been related to explosive spalling.

The addition of organic fibers that melt or shrink at temperatures at or below 149°C (300°F) may be used to vent the matrix to add protection from spalling at critical temperatures. A list of various fibers is given in Table III. It is important to consider both shrinkage and melting temperature in selecting fibers specifically for use with Alphabond.

To determine safe rates of heat input during firing precast parts, it is recommended that air temperature measurement be correlated with part temperature to govern firing schedules by embedding thermocouples both in the part and at its surface at the thickest cross section. Temperature difference between the part and free air should be closely controlled until the rate of water vapor release has safely diminished. For very thick sections, rates of between 1 to 2°C/hr (2° to 4°F/hr) until a uniform temperature minimum of 204°C (400°F) is attained have been employed successfully.

*Table III. Organic Fiber Types for Safely Dewatering Low- and No-cement Castables, typical length 0.64-2.5cm (1/4"-1")**

Composition	% Shrinkage (boiling water)	Temperature Effects —Comments
Acrylic	6.7	Sticks at 221-232°C (430-450°F)
Nylon	2.9	Melts at 215-221°C (419-430°F), decomposes at 316-382° C (600-720°F)
Polyester (regular tenacity)	9.0-11.0	Melts at 248-254°C, (478-490°F)
Polyester (high tenacity)	3.0-8.0	Melts at 248-254°C, (478-490°F)
Polyester (low shrinkage)	1.8-2.3	Melts at 248-254°C, (478-490°F)
Rayon	2.5-4.5	Decomposes at 177-240°C, (350-464°F)
Polyethylene/ Polyester (hybrid)	9.0-11.0	Sheath melts at 127°C (261°F), core at 248-254°C (478-490°F)
Polypropylene	1.4	Melts at 160-177°C, (320-350°F), decomposes at 288°C, (550°F)
Polyethylene	no data	Melts at 127-135°C, (261-275°F)

*Data courtesy of Mini Fibers, Inc.

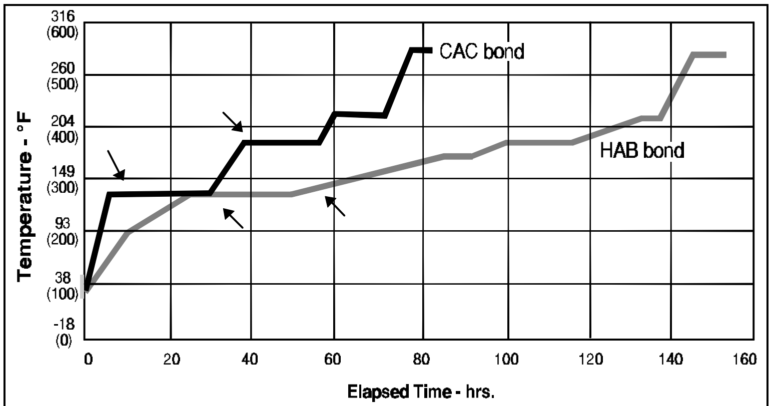


Figure 7. Firing schedule for a low cement castable precast shape containing HAB compared to CAC bonding agents. The two critical ramps for firing CACs that may lead to explosive spalling if applied to an HAB containing castable are marked with arrows.

Figure 7 gives an example of a typical Alphabond 100 castable firing curve for a large precast part containing Alphabond is compared to a curve for a part bonded with CAC. The Alphabond 100/castable firing curve shown may require further refinement to decrease total firing time and improve furnace turnaround time. This is offset by decreasing time to allow for "humidity" curing.

In Situ **Firing**

It is important to address *in situ* firing low permeability Alphabond-NCCs in the field with extreme care. This is because, even though a great deal of firing experience has been gained, firing rates may be difficult to control properly during the early stages. It should be noted that for dense LCCs containing CACs, explosive spalling is still prone to occur even though years of experience have been attained with these systems. It is also recommended that thermocouples be strategically located in the colder and hot face areas and in the mid-section of the refractory lining to better monitor and control rate of temperature increases during early stages of implementing the firing process. Using specialists or refractory manufacturers skilled in performing in situ firing of furnace linings is a cost effective option and is recommended for firing linings containing Alphabond.

It is essential, when firing thick cross sections, that sufficient cold face temperatures be reached that are beyond 204°C (400°F) and most of the water vapor is safely vented. Using firing schedules originally developed for firing calcium aluminate cement castables to fire castables with Alphabond has led to explosive spalling in firing thick precast parts and in situ firing walls in the field. A schedule used for firing thick precast parts similar to the one shown in Figure 7 may be developed. Conducting laboratory studies to determine safe firing rates for in situ fired parts or linings can be performed by using thick cross section test blocks to decrease the cost of experimenting with production parts and linings. Embedded thermocouples in several locations including colder locations should be used to control the firing process by correlating free air temperature and lining temperature.

Maximum Firing Conditions

For castables used in clean steel applications where minimizing moisture to control hydrogen pick-up is necessary, it is recommended that precast shapes be fired to temperatures exceeding 427°C (800°F). Studies performed on Alphabond or CAC bonded castables indicate that small amounts of moisture continue to release after treatment to 538-665°C (1000-1200°F) as shown in Figure 8.

Monolithics containing microsilica generally develop acceptable bond strengths after suitable treatment to 1093°C (2000°F). Higher temperature bonds then start to form at temperatures exceeding 1371°C (2500°F) where the Alphabond eventually reacts with the other fine ingredients in the matrix. This is demonstrated by sintering and in situ phases that occur when combinations of matrix materials are fired at various times and temperatures. Table IV lists XRD matrix phase development data for the constituents used in CALTAB 605A and 605S castable recipes.

As a result of heat treatment of the matrix, bond links between particles will consist of sintered amorphous silica, crystalline silica, alumina and mullite formation for CALTAB 605S with increasing temperature. From this data and photomicrographs, shown in Figures 9, 10, and 11, bonds develop as the matrix materials are heated progressively to higher temperatures. Silica-free compositions containing reactive aluminas will require treatment to temperatures exceeding 1371°C (2500°F) to develop equivalent strengths to microsilica containing castables and to CAC bonded silica-free castables.

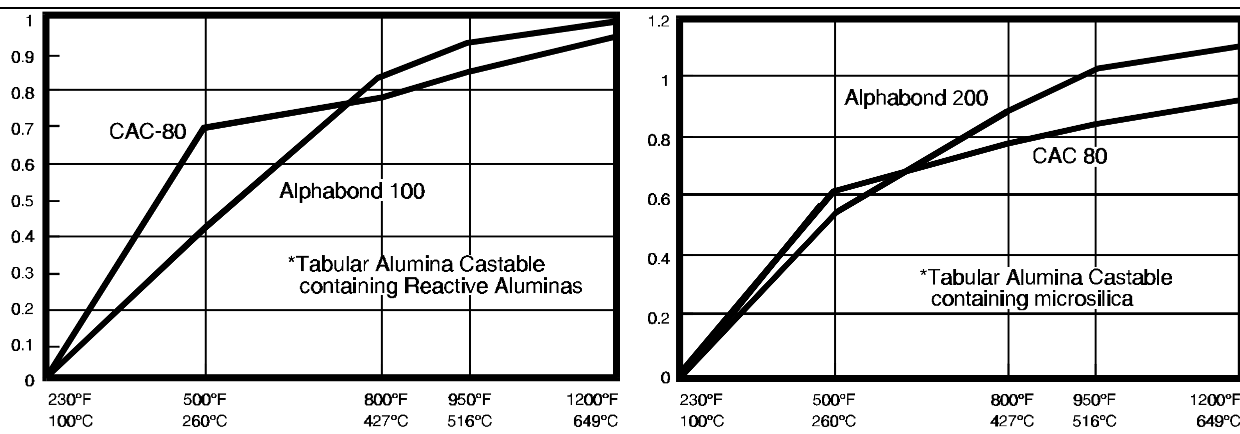
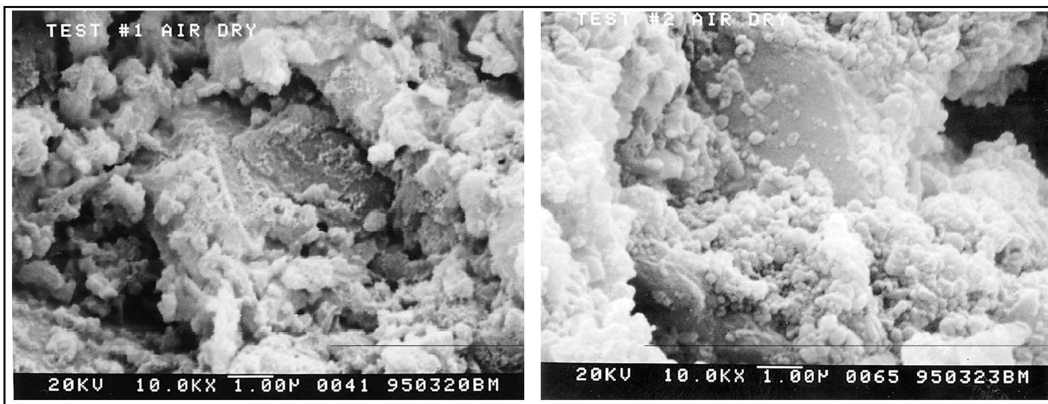


Figure 8. Comparative weight loss of low cement castables made with Alphabond 100, Alphabond 200, and CAC 80.

Table IV. Matrix Phase Development

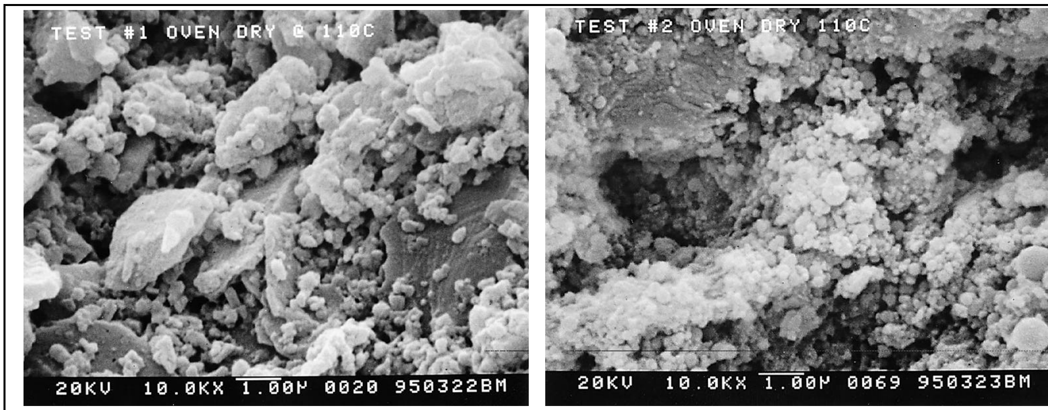
Matrix	Condition	Phases
HAB + Reactive Alumina (R.A.) (Alphabond 100)	Cured (20°C, 68°F)	Alpha Alumina Boehmite
HAB/S + R. A. + Microsilica (Alphabond 200)	Cured (20°C, 68°F)	Alpha Alumina Amorphous Silica Boehmite
HAB + R. A.	400°C (742°F)	Alpha Alumina Chi Alumina
HAB/S + R.A. + Microsilica	400°C (742°F)	Alpha Alumina Amorphous SiO_2 Chi Alumina
HAB + R.A.	1000°C (1832°F)	Alpha Alumina
HAB/S + R.A. + Microsilica	1000°C (1832°F)	Alpha Alumina Amorphous Silica
HAB + R.A.	1200°C (2192°F)	Alpha Alumina
HAB/S + R.A. + Microsilica	1200°C (2192°F)	Alpha Alumina Cristobalite
HAB + R.A.	1371°C (2500°F)	Alpha Alumina
HAB/S + R.A. + Microsilica	1371°C (2500°F)	Alpha Alumina Cristobalite
HAB/S + R.A. + Microsilica	1500°C(2732°F)	Alpha Alumina Mullite and Cristobalite



Fine aluminas

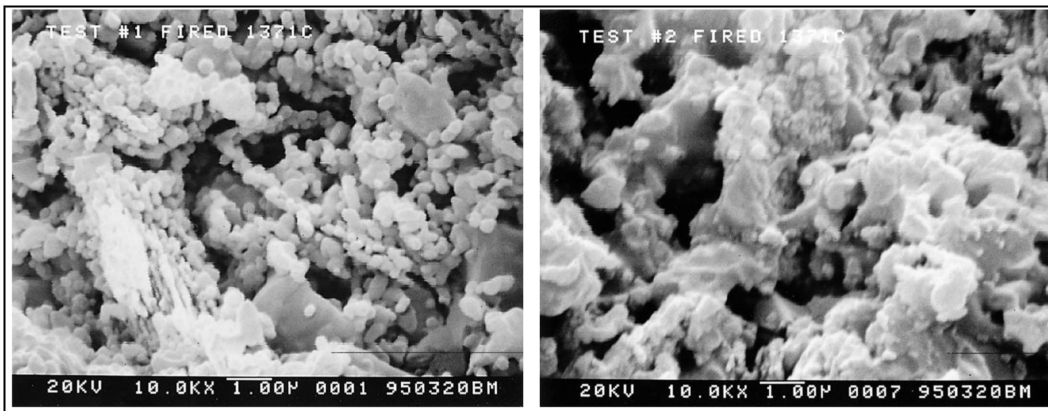
Fine aluminas and microsilicas

Figure 9. Comparison of fine refractory particles that adhere to Alphabond particles in a paste after air drying. This includes pastes containing either fine aluminas or fine aluminas and microsilica



Fine aluminas *Fine aluminas and microsilicas*

Figure 10. Comparison of fine refractory particles that adhere to Alphabond particles in a paste after drying at 110°C (230°F). This includes pastes containing either fine aluminas or fine aluminas and microsilica.



Fine aluminas *Fine aluminas and microsilicas*

Figure 1 Figure 11. Comparison of fine refractory particles that adhere to Alphabond particles in a paste after drying at 1371°C (2500°F). This includes pastes containing either fine aluminas or fine aluminas and microsilica. More agglomeration has occurred with the microsilica containing paste. Mullite was not observed via XRD until fired to 1500°C (2732°F).

Hot Strength and Thermal Shock

A 60% alumina castable recipe was used as a base for a test program to evaluate the relative impact of Alphabond 200 versus 70% CAC binders on HMOR and residual mechanical properties as a result of thermal cycling at 1204°C (2200°F). The composition of the following castable was selected because of extensive use of 60% alumina aggregates in a number of applications in high temperature industrial processes. The overall program consisted of thermal cycling prefired 17.8 x 2.5 x 2.5cm (7 x1 x 1") bars for 10 heat-up and air quench cycles (ASTM C-1171).

*M-60 Test Castable Recipe**

Composition Tyler Mesh	Weight %
4X8	35
8X20	15
20X50	10
-48	8
-200	20
microsilica	5
Alphabond 200 or CAC 70	7
water level	5.8 to 6.0 (good-ball-in-hand)

*This recipe is for demonstration purposes only. No warranty in specific applications is implied.

HMOR and fracture toughness at 1204° C (2200°F) were determined before and after thermal cycling on bars made from the same batch of castable. The bars had been prefired from 1109°C (2000°F) to 1510°C (2750°F) for 5 hours to simulate a pre-existing condition and phase maturation. Modulus of elasticity (MOE) was measured using a sonic resonance method on the bars before and after thermal shock to nondestructively determine relative degradation as a function of cycling. This data is summarized in Table V.

Bars bonded with Alphabond 200 that were prefired above 2500°F (1371°C) showed a marked increase in HMOR, residual strength, and fracture toughness over those bonded with CAC. Simulating iron and steel making conditions, it was observed that more bars containing Alphabond prefired at 1510°C (2750°F) survived thermal cycling without exhibiting the same level of catastrophic failure than bars bonded with CAC 70 which all failed.

Table V. Thermal Shock Effects on the M-60 recipe bonded with Alphabond 200 HAB versus bonded with 70% Alumina CAC

Binder/ Precondition Temperature[3]	HMOR, psi		Fracture Toughness[1], 2 psi x 1/2" in		Modulus of Elasticity[2] psi x106		Prism Spall
	Uncycled-1204°C (2200°F)	Cycled-1204°C (2200°F)	Uncycled -1204°C (2200°F)	Cycled-1204°C (2200°F)	Uncycled -1204°C (2200°F)	Cycled-1204°C (2200°F)	1204°C (2200°F)
HAB - 1093°C (2000°F)	20.8 (3030)	11.6 (1696)	1296	745	7.40	4.29	4 passed, 1 failed
CAC - 1093°C (2000°F)	5.9 (861)	9.8 (1435)	2004	630	7.81	4.18	5 passed
HAB - 1232°C (2250°F)	20.8 (3042)	11.5 (1674)	1323	759	8.58	3.87	5 passed
CAC - 1232°C (2250°F)	16.6 (2417)	11.0 (1606)	1053	709	8.12	4.36	4 passed, 1 failed
HAB - 1371°C (2500°F)	24.1 (3518)	15.1 (2200)	1535	964	9.07	3.94	5 passed
CAC - 1371°C (2500°F)	21.1 (3082)	5.7 (834)	1353	371	10.36	4.86	5 passed
HAB - 1510°C (2750°F)	41.0 (5993)	9.6 (1399)	2558	615	12.19	5.13	3 passed, 2 failed
CAC - 1510°C (2750 F)	25.5 (3727)	all failed	1657	all failed	12.42	all failed	5 failed

[1]ASTM C-1171 HMOR and Fracture Toughness at 1204°C (2200°F), 24 hr soak.
[2]Modulus of Elasticity determined by the sonic resonance method. mPa = psi ÷ 146.
[3]Soaked 5 hr.

Hot Deformation Studies

Sag tests were also conducted where 17.8 x 2.5 x 2.5cm (7 x1 x 1") 60% alumina bars were soaked at 1649°C (3000°F) for 5 hours. The level of deformation under their own weight on a 5 inch span was measured. The Alphabond 200 bonded bars sagged 2.2% while the CAC 70 bonded bars sagged 3.6%. These values correlate with relative HMOR values. This is indicative of improved creep and hot erosion resistance of the 60% alumina castable bonded with Alphabond.[6,7]

In Situ Spinel Formation using HABs

The development of in situ mullite phase provides benefits in improving mechanical properties and corrosion resistance of Alphabond 200 bonded materials containing microsilica. Similar concepts have been explored where magnesia or spinel are reacted with a fine alumina source to form in situ magnesium aluminate spinel that is silica and calcia free.[8] This will provide improved resistance to penetration and corrosion by iron, manganese, and calcia while increasing hot strength. One method described in this paper uses Alcoa's MR-66 magnesia-rich spinel to provide the spinel bonding by *in situ* reaction with fine calcines and with Alphabond 100 when exposed to sufficient temperature. To test this concept, various amounts of MR-66 spinel were added to a high alumina, tabular low cement castable (CALTAB 605A) and key properties determined.

Phase 1 consisted of applying MR-66 DIN70 in quantities ranging from 13.0 up to 23.1 weight % to the 605A. The recipes for these castables are in Table VI.

Table VI. In Situ Spinel Formation Trial Compositions

Mix	Composition	Casting Water, %	Daxad, %	MR-66 DIN70	lphabond, %	Fine Alumina		T-64 Tabular Alumina		
						A-1000 SGD	A-3000 FL	-325LI	-100C	Coarse
1	605A Std	5.65	0	0.0	5.0	5.0	5.0	10.0	10.0	65.0
2	1:1 Al_2O_3:MR-66	5.97	0	13.0	4.3	4.3	4.3	8.7	8.7	56.5
3	1:1.5 Al_2O_3:MR-66	6.39	0	18.3	4.1	4.1	4.1	8.2	8.2	53.1
4	1:2 Al_2O3:MR-66	7.36	0	23.1	3.9	3.9	3.9	7.7	7.7	50.0
5	605A Std	5.65	0	0.0	5.0	5.0	5.0	10.0	10.0	65.0
6	1:1 Al_2O_3:MR-66	6.08	0.013	13.0	4.3	4.3	4.3	8.7	8.7	56.5
7	1:1.5 Al_2O_3:MR-66	6.26	0.012	18.3	4.1	4.1	4.1	8.2	8.2	53.1
8	1:2 Al_2O_3:MR-66	7.02	0.012	23.1	3.9	3.9	3.9	7.7	7.7	50.0
9	1:2 Al_2O_3:MR-66 with 3.9%, 80% calcium aluminate cement	6.8	0.1	23.1	0	3.9	3.9	7.7	7.7	50.0

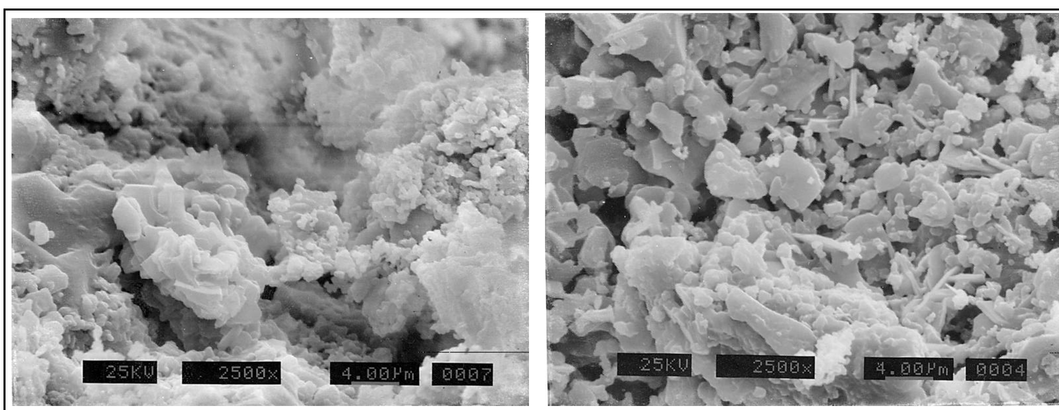
It was found in 25 x 25 x 175mm (1 x 1 x 7") bars that no cracking or excess shrinkage occurred via these admixtures and that sintering at 1500°C (2732°F) for 5 hours eliminated the presence of residual periclase in the MR-66 which fueled increased spinel formation in the matrix.

Phase 2 involved casting bars 25 x 25 x 175mm (1 x 1 x 7") composed of the CALTAB 605A composition with MR-66 DIN70 additions. Water demand was gauged for each mix and initial flow checked in addition to casting bars. The flow was very good compared to our standard 605A and working times suitable for demolding purposes. This was repeated using a dispersant to reduce water demand of the modified compositions and bars were cast for HMOR tests. Finally, a single batch was cast using 80% alumina calcium aluminate cement as the binder. All other mixes used Alphabond 100 as a binder.

All compositions cast very well with no obvious shrinkage away from the mold walls after the ambient temperature cure. No obvious fines separation occurred. There were no cracks visible to the eye in cured, dried, or fired bars. For the recipe containing 23.1% MR-66, some cracks occurred for thick sections after firing at temperatures up to 260°C (500°F).

HMOR values for the 13.0% and 18.3% compositions increased by ~50% (5.8 mPa, 842 psi, and 5.5 mPa, 798 psi) compared to the 605A standard composition (3.7 mPa, 536 psi). For the 23.1% composition, HMOR was approximately equal to the standard composition. The lower HMOR for the 23.1% composition could be a result of excess MR-66, lower percent HAB (3.9%), or drastically altered particle size distribution due to the addition of 23.1% MR-66 DIN70 MR-66.

SEMs of the microstructure of the standard and 13.0% MR-66 material at 2500X (Figure 12) show the relatively finer grained matrix structure achieved by making the admixture. This may contribute to the improved HMOR values. The relative success of adding magnesia rich spinel and resultant improvement in properties warrants further testing. This will consist of performing steel ladle slag tests on the standard material and recipes containing various levels of MR-66 admixtures bonded with Alphabond 100.



CALTAB 605A *CALTAB 605A/MR-66*

Figure 12. Microstructure of the standard CALTAB 605A (HAB) compared with that of the 13.0% MR-66 Spinel recipe. The latter has finer grain sized matrix

Application of Alphabond in Steel Plant Refractories

The successful implementation of Alphabond over CAC use in castables will be dictated by life performance levels achieved in the more severe applications. Many low temperature applications may not justify the use of castables with Alphabond because of their lower bond strength as a result of exposure to those conditions. However, sintering aids could broaden the possibilities of using Alphabond at lower temperatures. This section of the paper describes some applications that represent severe conditions that exist in the steel industry where castables containing Alphabond are proven or could be used.

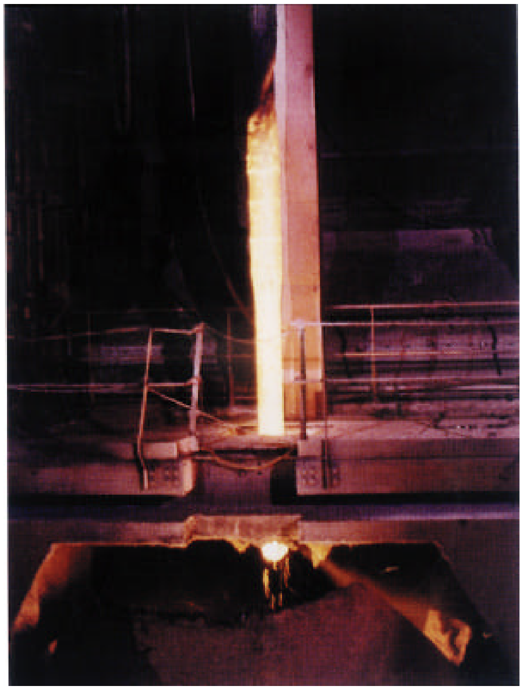
Injection Lances

One of the most severe applications for a refractory is on injection lances for ladles. The refractory covering feed pipes in injection lances must withstand being plunged through basic slag into liquid steel superheated to 1649°C (3000°F) and remain immersed in the steel while solid agents or gasses are injected into the metal. Then the lance is removed and the refractory rapidly cools while on standby for the next cycle.

Two lances on standby are shown in Figures 13 and 14. The lance pictured in Figure 13 shows the refractory tapering from slag corrosion.

Figure 13. A refractory-covered lance used for injecting desulphurizing agents and gases into molten iron and steel to improve metal quality. The refractory experiences both thermal shock and corrosion by slags as evidenced by the neck down in the zone

The lance shown in Figure 14 exhibits superior resistance to slag corrosion. Alphabond is currently being used in this application in both bauxitic and high alumina, low binder castables. Life for a lance is usually expressed in terms of total exposure time in the metal and numbers of operating cycles. The trend toward increasing injection time to attain further improvements in metal quality is pressing the need for superior refractory castable materials. The superior thermal shock resistance and corrosion



resistance of Alphabond in many compositions have contributed to significant improvements in lance life. Further improvements could be attained using both *in situ* and aggregate admixtures in tabular alumina recipes. This is, in part, dependent on the degree of cooling that protects the steel feed pipe during use and standby.

Figure 14. Another lance just as it is removed from the ladle. The necked-down region did not occur on this lance. Alphabond along with magnesium aluminate spinel in the castable will improve slag and thermal shock resistance.

Delta Sections

Precast electric furnace delta sections must withstand both the thermal extremes associated with radiant heating from the electrodes and corrosion by lime and slag. These carefully fired large shapes (up to 6 metric tons), have exhibited markedly improved refractory life when Alphabond is used in lieu of CACs. Figure 15 illustrates the size and shape of one of these large components.

Figure 15. A precast electric furnace delta section 20 inches thick. Significant improvements in life have been observed with castables which contain Alphabond; however, these sections must be fired carefully to avoid explosive spalling.

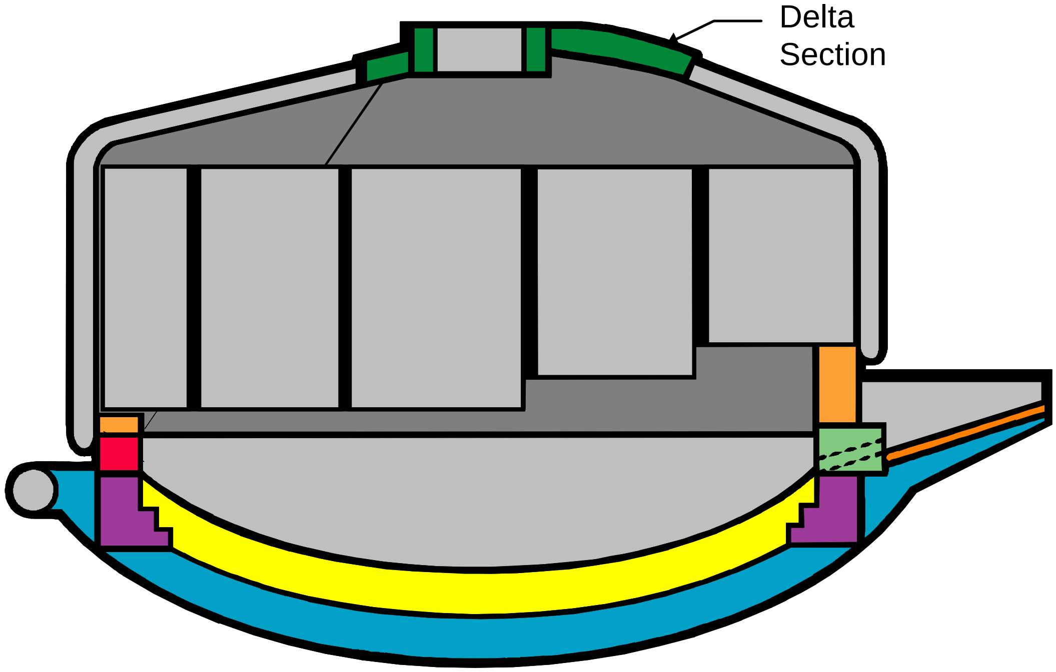


Figure 16. Cross section of a modern electric furnace showing the location of the delta section. (Source: Harbison Walker Refractory Company "Modern Refractory Practices.")

Figures 16 and 17 show the location of a delta section in an electric furnace. The section must resist high temperature thermal cycling and corrosion from lime and slag splash. During fabrication, delta sections are usually cast in more than one pour.

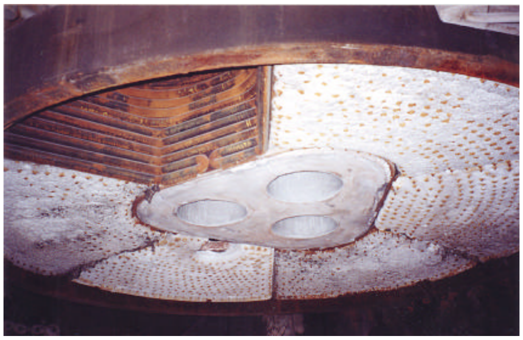


Figure 17. An electric furnace delta section shortly before operation.

Because Alphabonds are mixed and cast using equipment and procedures similar to those used for castables containing CACs, substitution of those materials is accomplished with limited reformulation in many cases. Firing schedules for delta sections up to 51cm (20 inches) thick should be performed very carefully to minimize chances of explosive spalling. (See Figure 17 for a typical example.) Once the part has been uniformly heated to a temperature of at least 204°C (400°F), firing may be carefully expedited to minimize impact on furnace turnaround time.

Degasser Snorkels

Unlike lances, RH and DH degasser snorkels have no direct means of providing cooling to the supporting structure. Therefore, structural deformation, thermal shock, and corrosion greatly impact the life of these components. Generally, they are composed of tabular alumina aggregates to obtain maximum residual strength and integrity after a number of thermal cycles. Corrosion by slags may become an issue for high alumina castables, especially slags containing high levels of iron and manganese oxides. To further resist corrosion, Alphabonds have been successfully used to bond spinel aggregates in castables. Typical snorkels for the RH degasser are shown in Figure 18. Alphabond containing castables for these components must be carefully fired to avoid explosive spall. This is because time-temperature ramps will be more difficult to control than for precast shapes in programmable furnaces.

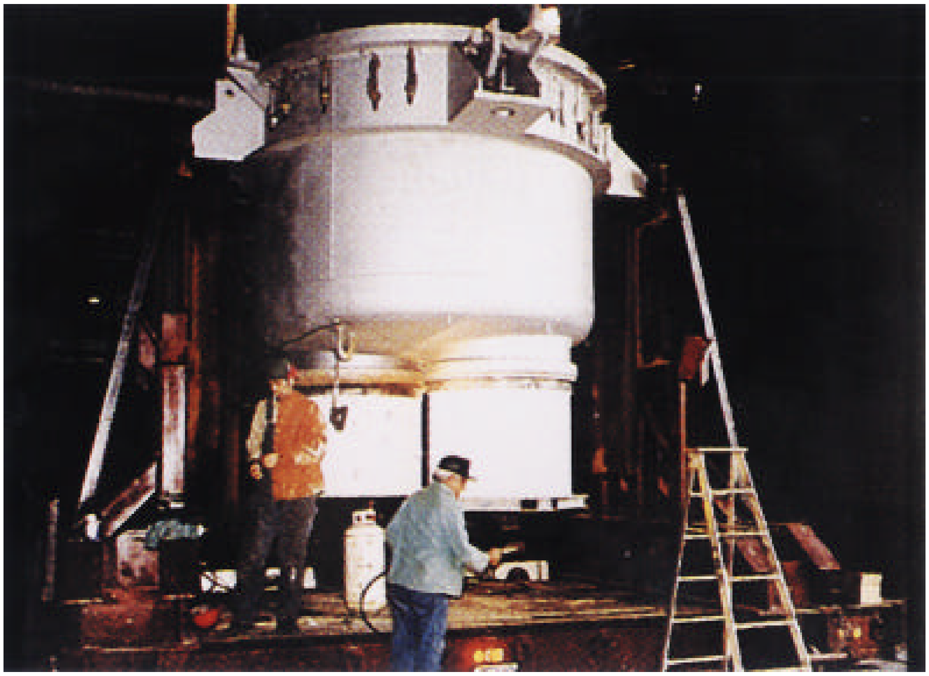


Figure 18. Alphabond in a tabular alumina castable degasser snorkel would improve life through increased thermal shock resistance. However, careful control of firing schedules in the steel plant is essential to avoid explosive spalling.

Precast Ladle Impact Pads

A cross section of a modern steel ladle is shown in Figure 19.

A precast ladle impact pad, photographed while on standby, is shown in Figure 20. These shapes withstand the extremes of thermal shock, metal and slag erosion, and impact from the initial contact with the metal stream. The composition of the pour pad castable was a 70% alumina material bonded with Alphabond 200. The cross section of the pour pad, shown in Figure 21, revealed that the overall thickness had decreased from 30.5 to 22.5 cm (12 to 9 inches) during a typical campaign.

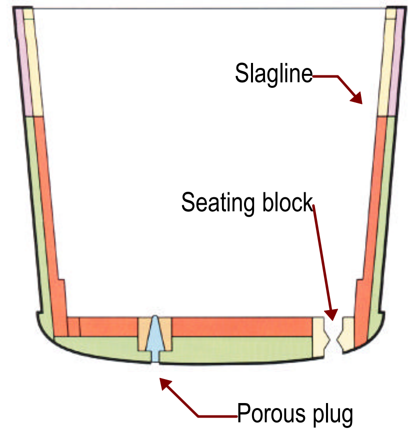


Figure 19. Cross section of a steel ladle. (Source: Harbison Walker Refractory Company "Modern Refractory Practices.")

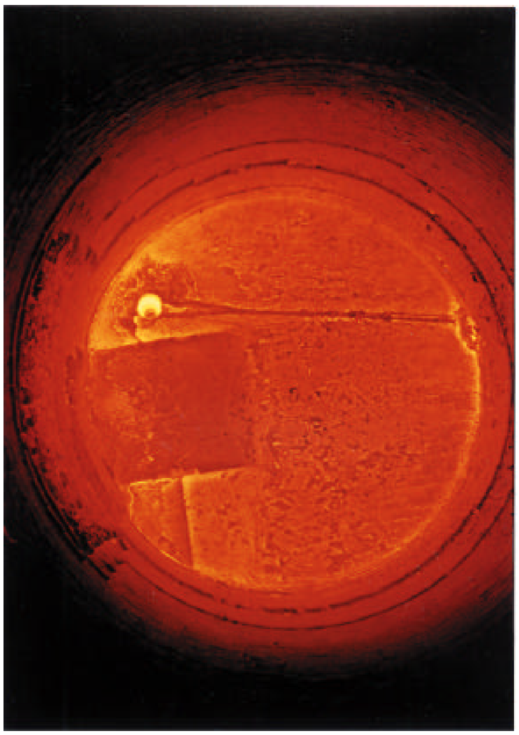


Figure 20. A precast impact pad balances the wear in ladle bottoms by taking the full brunt of the initial metal stream.

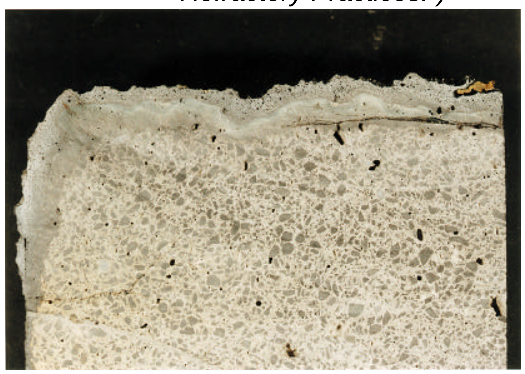


Figure 21. Cross sectional cut of the postmortem sample from a 70% alumina precast ladle impact pad. The degree of attack by slag decreases rapidly from the altered hot-face into the original refractory. A fracture line segregates the totally and partially altered material. Corrosion occurred on the top of the specimen (shown here) and on the original edge of the shape because the joint between it and the surrounding brickwork opened exposing the edge to slag.

Photos and field observations all point out that corrosion of the pad was not the primary mode of failure. Termination of service occurred because the pad had actually fractured, possibly on initial heats which was caused by tremendous impact of the liquid steel on the pad. The cracking was followed by penetration of steel around the edges of the pad due to loose brickwork making up the remainder of the ladle bottom. This allowed post mortem of a component which had not been completely consumed by corrosion to study the wear mechanisms.

There are four major zones accompanying the corrosion of the specimen. A slag-rich zone, a fully altered zone, a partially altered zone (Figure 22) and finally, the unaltered refractory (Figure 23). Visual examination of the specimen revealed that the outermost refractory zone was completely reacted with slag and as a result of development of intermediate phases, spalling occurred in thin layers probably as a function the number of heats.

A crack separates the more fully altered zone from the preserved regions indicating that a significant mismatch occurred between adjacent corroded and unaltered zones. Detailed SEM studies including EDX elemental analysis were used to determine the extent of corrosion and penetration in the underlying layers of the refractory by detecting relative levels of corroding agents: iron, silicon, calcium, and manganese that are associated with steel making slags.

The depth of penetration and alteration were used as measures of the contribution to corrosion control exhibited by Alphabond. It was found that the Alphabond containing matrix had successfully arrested penetration by calcium, manganese and iron by surrounding and protecting aggregates from corrosion. Further improvements may be attained by adding spinel to tabular castables bonded with Alphabond.

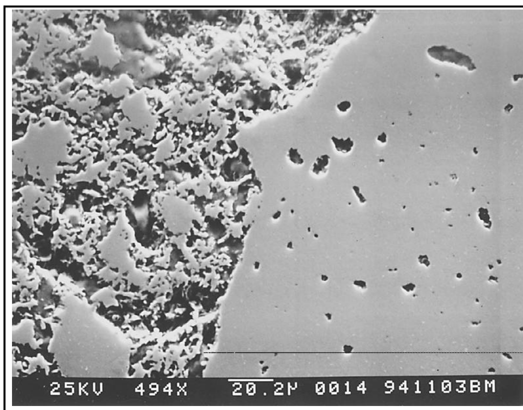


Figure 22. This photo shows partially altered refractory. Elemental analysis shows slightly higher levels of calcia and iron oxide. Relics of the original aggregate and surrounding matrix are visible.

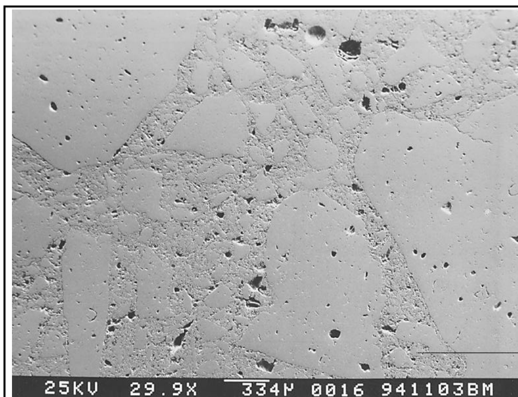


Figure 23. SEM photo of the original refractory showing calcined high alumina aggregate and surrounding matrix materials. EDX analysis shows essentially no corrosive elements present. This is indicative of the level of contribution of the Alphabond toward controlling corrosion.

Continuous Caster Tundish Shapes

A cross section of a modern continuous caster tundish, shown in Figure 24, illustrates precast components used to suppress initial splashing and control flow during long casting sequences. This includes dams, weirs, and impact pads. Alphabond is used as a binder in these shapes to improve thermal shock and erosion resistance and to improve hot strength.

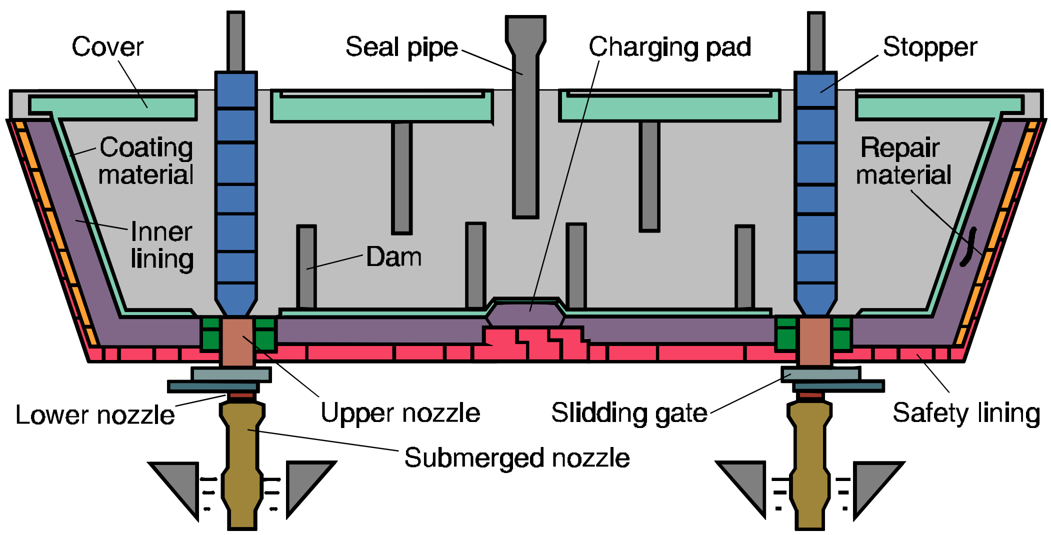


Figure 24. Alphabond used in Precast shapes in tundishes enhance erosion resistance and hot strength.

Castable Demonstrations

Vibratable and self flow compositions have been developed for field demonstrations using castables containing Alphabond. Their formulations compared to those for CALTAB 605A and 605S are given in Table VI. The vibratable recipe exhibits flow similar to CAC bonded tabular castables with 4.0% water.

Table VI. Tabular Alumina Test Recipes for Demonstrating Alphabond 100 and Alphabond 200 Binders, %

Raw Materials	605A	605S	Self Flow	Vibratable
Tabular Alumina T-64				
1/4x8	0	0	35	0
3x6	0	0	0	26
6x10	16	16	0	5
8x14	12	12	10	9
14x28	12	12	10	14
28x48	15	15	5	11
48x200	10	10	5	8
-100C	10	10	0	0
- 325	10	10	0	0
-20 micron B	0	0	19	10
Reactive Aluminas				
A-3000FL	5	5	10	8
A-1000SGD	5	0	0	3
Microsilica	0	5	3	3
Alphabond 100	5	0	0	0
Alphabond 200	0	5	3	3
Water (D.I.)	5.4	5.4	5.3-5.6	4.0
Admixtures	0	0	yes	yes

Demonstrations of the self flow mix using Alphabond 200 for a binder have been performed using the flow box which is shown in Figure 25. Good initial self flow is defined by the time required for the mix contained in the reservoir, with only the aid of gravitational force, to flow to the opposite end of the box and completely level to its maximum height as shown in Figure 25. Self leveling should occur within 30 seconds and, for an optimum castable, uniformly self level to a 25 mm (1 inch) height. Acceptable flow decay is defined by the time required for the castable to attain optimum flow and self leveling after a period of 15 minutes has elapsed after mixing water with castable. Self leveling should occur within 2 minutes.

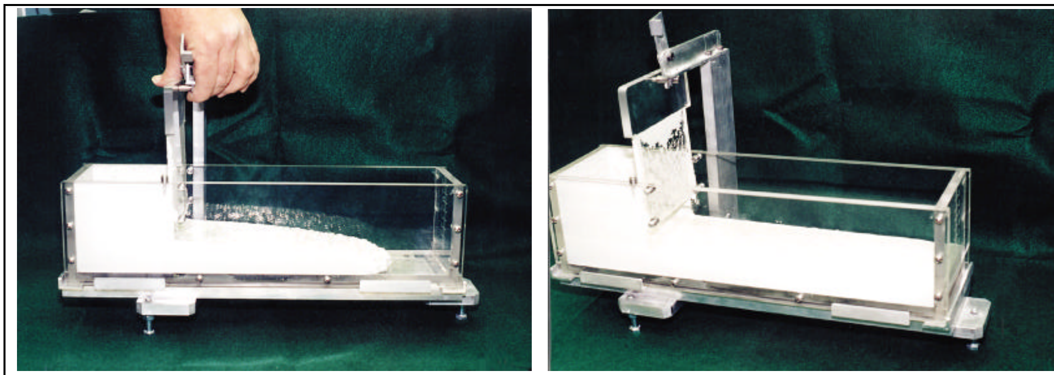


Figure 25. Flow box used to quantitatively determine the decay of self-flow properties of a castable from initial values.

Some initial flow data as a function of casting water level is shown in Table VII for a tabular based castable bonded with Alphabond 200.

Table VII. Self Flow Demonstration Data—Alphabond 200 Castable

% Water	Height (mm)	Time (seconds)	Time after Mixing (min.)
5.5	23	14.3	5 (initial)
5.3	22	15.9	5 (initial)
5.1	21	20.0	5 (initial)
5.1	20	40.0	15

The castable containing Alphabond 200 exhibits relatively good flow and flow decay properties with only 5.1% water. Admixtures used to achieve these flow rates were sodium hexametaphosphate (SHMP) at a level of 0.015 weight % and citric acid at a level of 0.006 weight % (based on mix weight).

Conclusions

This paper summarizes important practical aspects associated with using Alphabond hydratable alumina binders in high performance castable compositions. This includes information important for batching, mixing, casting, setting, and firing these castables. Data is provided that gives some concepts needed to develop firing schedules to assist in avoiding explosive spalling thick sections. Also, basic data is presented that will enable optimization of strength by understanding effects of heat treatment on thorough dewatering and bond development through the development of *in situ* mullite and spinel phases.

In summary, the differences and advantages of using Alphabond compared to CACs in castables are the following:

1. Data and suggestions are presented that will decrease the risk of explosive spalling low permeability castables using Alphabond for binders for shops previously using CACs. For example, organic fiber options, TGA/TGA' data, and typical firing schedules for thick parts.
2. Improved HMOR and fracture toughness result when using Alphabond in high alumina (60% alumina) recipes fired at temperatures exceeding 1371°C (2500°F).
3. Decrease in silica that could contribute oxygen to liquid steel will result for microsilica containing CAC castables after exposure to temperatures exceeding 1500°C (2732°F) by formation of in situ mullite via reaction with Alphabond.
4. Elimination of calcium that could contaminate molten high purity alloys in vacuum melting will result for silica-free, mullite, or spinel bonded high aluminas.
5. Examples of using Alphabond in castables in steel making applications have demonstrated success in components that see exposure to severe conditions in the field (for example, lances, impact pads) where controlling slag resistance, hot erosion, impact, and thermal shock resistance are important. This is in light of increasingly severe conditions being imposed on these refractories exposed to intensive clean steel refining process conditions needed to produce modern steel and superalloy products.[9,10]
6. A new concept of using in situ spinel formation where various levels of magnesia rich spinel MR-66 were successfully incorporated into a high alumina, silica free castable bonded with Alphabond. A range of recipes demonstrating good flow and working time properties exhibited 50% HMOR improvement over the all-alumina system.

7. Castable compositions are included for self flow and vibratable recipes using Alphabond 100 and Alphabond 200 for field demonstrations that will broaden the ways high performance castables are installed and types of components that can be fabricated. Alphabond containing high alumina no-cement castables with fumed silica and silica free recipes have demonstrated excellent self flow characteristics.
8. In a number of cases, Alphabond binders may be directly substituted for CACs in a wide variety of castable recipes.

Acknowledgments

Appreciation is extended to these major contributors:

A. L. Maynard, N. Mills, R. W. McConnell,
Applications Laboratory, Bauxite, AR

J. A. Cole, R. M. Frye,
Alcoa Vidalia, LA Operations

R. M. Dunlap, R. Kois, B. L. McCormick, R. A. Marra,
R. L. Ross
Alcoa Technical Center, PA

G. W. Kriechbaum
Frankfurt, Germany, Alcoa Industrial Chemicals—Europe.

Biographies

M. William (Bill) Vance

M. William (Bill) Vance is Application and Market Development Manager—Refractories, Alcoa Industrial Chemicals, Pittsburgh, PA. He has extensive experience in refractory applications in the iron and steel and aluminum industries. He is responsible for all refractory market development and customer application support for North America.

Bill has authored and co-authored technical papers regarding ceramics for the space shuttle thermal protection system and refractories for steel plant applications including: continuous caster refractories, degasser refractories, reheat furnace skid-pipe insulations, light-weight gunning materials, ceramic recuperators and ceramic fiber insulations. He also conducted exploratory research in ceramic steel filtration systems. He has six patents on steel plant refractories and aerospace ceramics.

He is a member and past chairman of the Pittsburgh Section of The American Ceramic Society, a member of the Refractories Division, ACerS, and Sigma Xi. Bill graduated from UMR in 1965/67 with BS/MS degrees in Ceramic Engineering.

Kenneth J. Moody

Kenneth J. Moody is currently Applications Manager Alcoa Industrial Chemicals, Aluminum Company of America (ALCOA). He obtained his B.S. degree in Ceramic Engineering in 1975 from Clemson University, Clemson, South Carolina.

During his career, Mr. Moody has worked in the product development of calcium aluminate cements, refractory castables, insulating firebrick and gunning castables as Product Manager for the castable line at Babcock and Wilcox Refractories Division (currently Morgan Thermal Ceramics).

Prior work experiences included Research, Application and Technical Service assignments associated with calcium aluminate cement products while at Lone Star Lafarge Calcium Aluminates, Inc. Before becoming Market Manager for Refractory Markets for ALCOA Industrial Chemicals Division, Mr. Moody held positions as Application and Market Development Manager—Ceramics/Abrasives, as Application and Market Development Manager—Refractories and most recently, as Manager, Applications and Market Development for abrasives, ceramics and refractories.

References

1. ASTM C401
2. Alcoa Industrial Chemicals Product Data Sheet No. CHE 955, “Alphabond 100 Hydratable Alumina Binder”, Sept. 1994, F35-15513.
3. Alcoa Industrial Chemicals Product Data Sheet No. CHE 955A, “Alphabond 200 Hydratable Alumina Binder”, Sept. 1994, F35-15514.
4. Alcoa Industrial Chemicals Product Data Bulletin, “Alphabond 100 and 200 Hydratable Alumina Binders—Recommendations for Application and Use”, Nov. 1994, F35-15516.
5. Alcoa Industrial Chemicals Product Data Bulletin No. 2, “Alphabond 100 and 200 Hydratable Alumina Binders—Suggested Setting, Drying and Firing Procedures”, Dec. 1994, F35-15618.
6. G. W. Kriechbaum, V. Gnauck, G. Routschka, “The Influence of SiO_2 and Spinel on the Hot Properties of High Alumina Low Cement Castable”,

Proceedings: no testVII International Colloquium on Refractories, October 6-7, 1994, Aachen, Germany, p. 150-159.

7. M. Strothman, et al., “High-Temperature Performance of Cement-Free and Low-Cement Alumina Castables”, Proceedings 1995 UNITECR Conference, Kyoto, Japan, Nov. 19-22, 1995.
8. M. W. Vance, G. W. Kriechbaum, R. A. Henrichsen, G. MacZura, K. J. Moody, and S. Munding, “Influence of Spinel Additives on High Alumina/Spinel Castables”, American Ceramic Society Bulletin, Vol. 73, No. 11, Nov. 1994, pp. 70-74.
9. S. Asano, “Steelmaking Refractories in Japan—Now and Fugure”, Shinagowa Technical Report, Vol. 33, 1990, pp. 61-67.
10. G. Provost and C. Gatellier, “Impact of Refractory Products on Steel Quality and Inclusionary Cleanliness”, Proceedings: no testVII International Colloguium on Refractories, October 6-7, 1994, Aachen, Germany.

Alcoa Industrial Chemicals

P.O. Box 300, 4701 Alcoa Road, Bauxite, AR 72011, USA

Phone: (800) 643-8771
Fax: (800) 874-0481
E-mail: baucc01.alcoa02@ssw.alcoa.com

For calls outside of the U.S.: Phone: (501) 776-4949, *Fax:* (501) 776-4762