

Latest Development in Refractory Monolithics

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ABSTRACT

The steel ladle is one of the highest refractory consumption areas in steel making and it has been constantly requiring improvements of refractory lining concepts due to the increasingly demanding process conditions to improve steel quality.

Various trends in refractory monolithics for steel ladles are discussed; giving a focus on their properties and performance based on different raw materials with emphasis on advantages of highly pure synthetic ones.

INTRODUCTION

The world demand for high quality steel requires extended treatment of the steel in the steel ladle. This has a remarkable impact on the steel ladle refractories, e.g. the need for high functional refractories. Operational changes such as increasing tapping temperatures, longer hold times and more aggressive secondary metallurgy are countered by the need for thinner refractory linings and longer refractory life.

Based on that, steel ladle lining represents an important cost factor in steel not only for refractory cost itself, but mainly for operational cost, e.g. production losses due to relining, vessel unavailability, incidents and lack of reliability. In a recent congress in Brazil one of largest global integrated steel producers in the world, who produces on average over 100 millions metric ton per year reports that steel ladles represent around 30% of refractory expenses from total of steel shop 76%. In addition, environmental, safety and employees health aspects are also taken into consideration nowadays.

Finally, the guarantee of refractory quality and security supply, in the current scenario of shortage mainly concerning natural refractory raw materials, have drastically propelled the demand for synthetic raw materials.

The combination of the several factors above has led to increase the importance and interest for monolithic refractories. In this paper the main trends in steel ladle lining in Europe will be reviewed with a focus on monolithics and recent monolithic refractory property improvements based on synthetic raw material advantages.

TRENDS IN STEEL LADLE LINING IN EUROPE

The monolithics market in Europe as other regions around the world is facing many of the same pressures as the refractory brick industry. An extreme dependence on it used to be the low Chinese raw materials cost and its current shortage. Followed by continue consumers requirements to reduce installation downtime and refractory consumption per ton of steel production.

On the other hand, as mentioned before, the demand for higher purity grade steel is increasing and the proportion of secondary refining for steel is heightened, thus requiring quite severe operation conditions for steel ladles such as:

- Increased tapping temperatures or introduction of ladle furnace;
- Longer holding times;
- Higher purging efficiency;
- Increased chemical and physical attack.

As countermeasures, and to support the continue production demand, many steelworks are increasing the ladle capacity reducing the ladle thickness lining, adjusting or changing ladle lining and switching to higher quality refractory grades.

SYNTHETIC VS. NATURAL AGGREGATES

For high alumina refractories in steel ladles a change is ongoing from naturally based refractory aggregates such as andalusite or bauxite to synthetic ones like tabular alumina and spinel. This applies to both monolithic and brick linings. The higher purity synthetic aggregates provide better performance with regard to lining life, steel cleanliness, refractory unit consumption per tonnage of steel and, as a general rule, more predictable behaviour. Just doing a quick review on the memories of a very important European annual seminar, it was found that in the year 2000 seven steelworks reported steel ladles lined with bauxite and andalusite. In 2006, only one steelwork was still remaining with bauxite brick lining, and it changed to AluMagCarbon bricks in 2008.

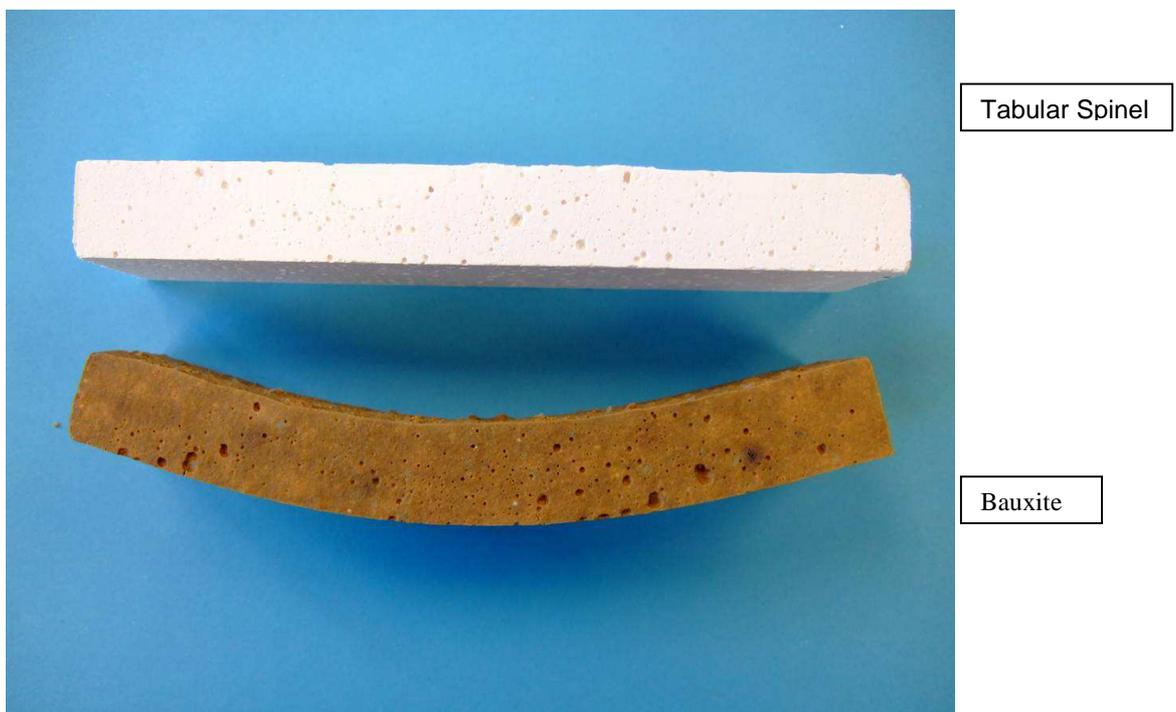
In Table 1 below, the chemical analysis results of main alumina raw materials source used as aggregates in steel ladle refractory lining are shown:

Table 1 – Chemical Analysis and bulk density comparisons of synthetics vs. natural alumina aggregates

Wt.%	Andalusite	Bauxite	Brown fused alumina	Tabular alumina	Spinel AR78 AR90
Al ₂ O ₃	56-59	85-90	94-97	>99.4	>99 (+MgO)
SiO ₂	38-40	5-10	0.8-1.5	<0.09	<0.18
TiO ₂	0.2-0.5	3-4	1.5-2.5	<0.01	<0.01
Fe ₂ O ₃	0.8-1.5	1-2	0.15-0.5	<0.04	<0.25
Earth alk.	0.1-0.3	0.4-0.8	0.4-0.6	<0.05	<0.3 (CaO)
Alkalis	0.2-0.8	0.2-0.8	0.2-0.4	<0.4	<0.2
BD [g/cm ³]	3.1	3.1-3.4	3.7-3.8	3.55	3.3/3.4

It is evident that in synthetic alumina based aggregates tabular alumina and AR spinel very low percentages of impurities like SiO_2 and TiO_2 are present, as well as alkalis that are fundamentally known to reduce refractoriness. To demonstrate this in a simple and qualitative way, Almatis performed a Sag test with low cement castables (LCC). The first one is based on Tabular and Spinel aggregates and the second one is based on Bauxite. The sample bars with dimensions of 160x40x20mm were placed in the furnace for 5h at 1550°C, being supported at both ends. Figure 1 shows that the sample based on tabular/spinel is still completely flat and the sample based on bauxite is completely warped.

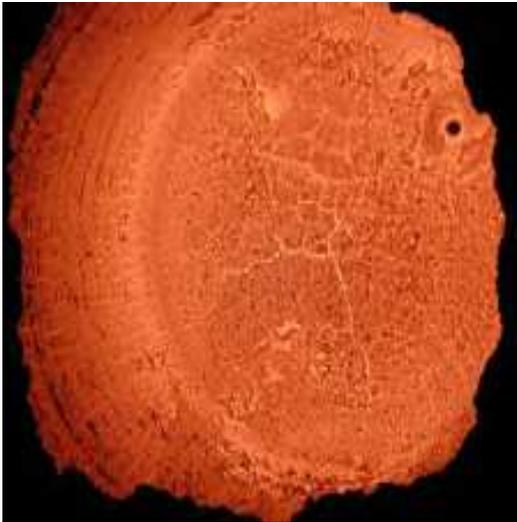
Figure 1 – Sag test of LCC's castables



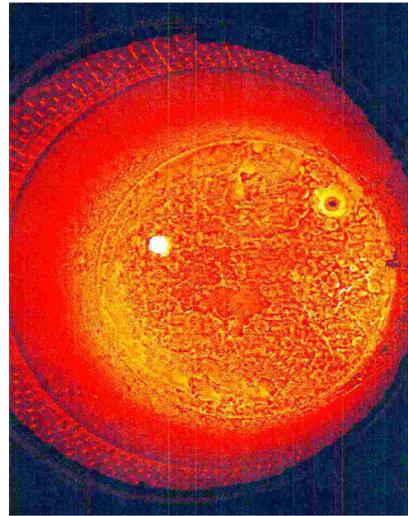
Sag test of castable at 1550°C / 5 h

A recent trend for monolithic ladles bottom is the use of coarse size aggregates. The new coarse size tabular aggregate 6-15mm was introduced, giving an additional advantage to castables by decreasing crack formation, as exemplified in Figure 2.

Figure 2: Recent Trend: coarse sized aggregate (6-15mm) for ladle bottom castables



Left: 6mm top size castable – Typical crack formation for large monolithics

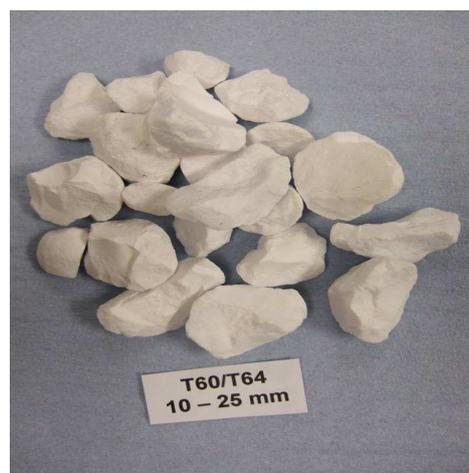
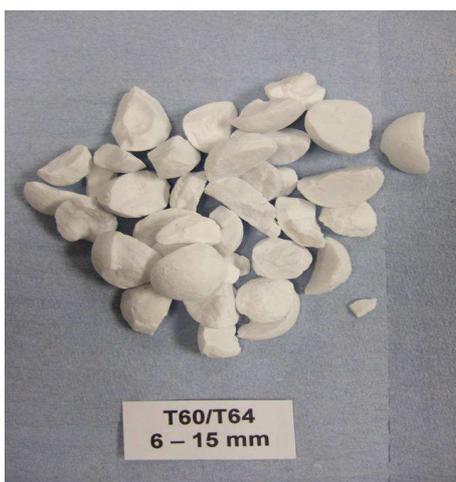


Right: 15mm top size \Rightarrow no cracks

Both tabular alumina based castables

As a recent development product Almatix has just launched the new generation of coarser size 10-25mm tabular alumina as shown in Figure 3 below, providing less castable water demand, lower open porosity and reduction in matrix fines. As a general rule, matrix fines are the most expensive fraction of any castables.

Figure 3: Tabular Alumina coarse sizes – regular product 6-15mm and development product 10 - 25mm



SPINEL CONTAINING AND SPINEL FORMING CASTABLES

Magnesium aluminate spinel is a member of a group of oxides that have the same crystal structure, which is named the spinel structure. The spinel group contains over twenty members, but only a few are considered common. The general formula of the spinel group is AB_2O_4 , where A represents a divalent metal ion, such as magnesium, iron, nickel, manganese and/or zinc, and B represents trivalent metal ions such as aluminum, iron, chromium or manganese. Unless otherwise described, the term “spinel” in this paper will refer to $MgAl_2O_4$, the mineral spinel, which is the only compound in the binary system $MgO - Al_2O_3$.

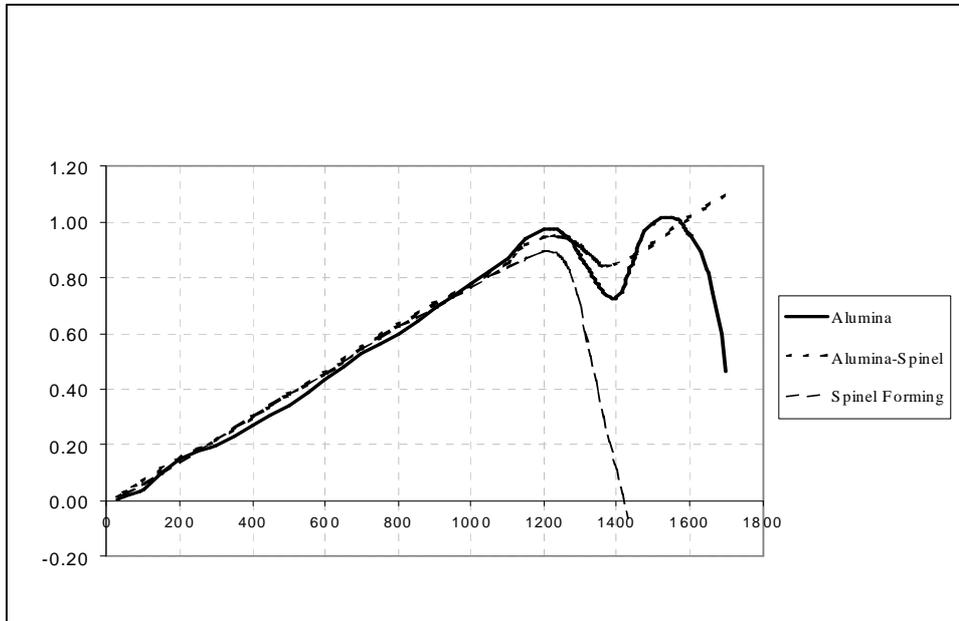
There are several examples where in-situ spinel formation is formulated as part of the castable, possibly to reduce cost, however, there are significant disadvantages to this approach. The formation of spinel from alumina and magnesia leads to a remarkable volume expansion. Theoretically, this volume expansion will be 13%, based on a relative density calculation. In practice, however, this expansion is around 5%, still excessive for the microstructure to accommodate without cracking. Addition of fine silica, such as silica fume, is often used to promote liquid-phase sintering and to allow some local deformation to overcome the volume expansion. However, the residual glassy phase will have a significant effect on the hot strength, as seen in Table 2.

Table 2 - Effect of pre-reacted spinel vs. in-situ spinel on thermo mechanical properties (RUL= Refractoriness under Load @ 0.2 MPa)

	Self-flow LCC Tabular Alumina	Self-Flow LCC Alumina-spinel	Self-flow ULCC Spinel forming
Chemistry (wt %)			
Al ₂ O ₃	98	93	92
MgO		5	6.4
SiO ₂	< 0.05	< 0.05	0.5
CaO	1.5	1.5	0.7
Mixing Water (%)	5.0	5.3	5.0
HMoR @ 1500C (MPa)	17	23	2
RUL			
Max Def (Dmax) (%)	1.02	1.10	1.24
T @ Dmax (C)	1540	1700	1250
T 0.5% (C)	1690	> 1700	1360
T 2% (C)	> 1700	> 1700	1655

The effect of spinel addition and the use of silica fume on the thermo mechanical properties can be more dramatically seen graphically, as shown in Figure 4:

Figure 4 – Refractoriness under load 0.2MPa, pre-fired at 1000°C



In a ladle sidewall, spinel-forming castables shows some benefits. The volume expansion due to in-situ spinel formation is said to contribute to a densification of the surface layer. Also, the liquid phase formation due to silica addition increases the mechanical flexibility of the castable, which can be beneficial to avoid cracking of the lining during pick-up and set-down of the hot ladle. In general, because ladle sidewalls are less subject to erosion than a ladle bottom, the lower hot strength of the in-situ castable is less of a factor. However, poor tapping practices and/or extensive stirring can cause significant higher sidewall erosion, and spinel-forming refractories with high silica contents will then exhibit higher erosion rates.

For pre-cast shapes, spinel-forming formulations are not preferred due to hydration of the magnesia additive. Also, many pre-cast shapes are used in areas of high erosion such as impact areas, purging plugs and well blocks. The reduced erosion resistance of in-situ spinel formulations will reduce the life and increase operating cost.

Recently, with a combination of pre-formed spinel and in situ spinel, improvements were obtained on the following castable properties:

- Working time
- Flow behavior
- Permanent linear change
- Hot properties

In cement bonded spinel forming castables (alumina-magnesia), the fume additions lower the temperature to onset of melting from around 1800°C to below 1400°C. Therefore, cement free castables are an interesting alternative. When calcium aluminate cement is replaced by the calcia free Alphasbond binder, the temperature of onset of melting is increased from below 1400°C to 1578°C. The consumption of Alphasbond is increasing remarkably in the last years, and it is often used in spinel forming materials.

MATRIX IMPROVEMENTS BY ALUMINA FINES

The three main internal components of most monolithics refractories are the coarse aggregate, fine aggregate and matrix. Going to in more details on the three components, named *refractory solution*, coarse aggregate is basically the brick that forms the foundation, fine aggregates fill the intermediate voids between the coarse aggregate and the matrix fines include very fine mineral, binders and additives.

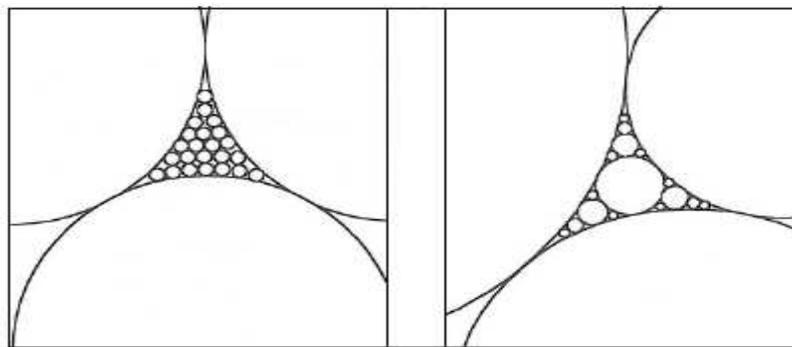


Figure 5 - Refractory particle packing

The fourth component that has the same or more importance is the installation method. All of them work together to provide the strength and refractoriness of the monolithic, but matrix fines have a determinant influence on water demand, rheology, green and final strength and setting time. Indeed the different Calcined Alumina fine grade can remarkably improve most monolithic characteristics.

In the 1990's the main focus in monolithic development was on the reduction of water demand of the castables. This is important because it is well known that 1% additional water will result in about 3% higher open porosity of a tabular alumina castable after drying; this, in turn, reduces the wear resistance of the lining. Low soda, small crystal size and fully ground reactive aluminas along with high performance additives such as dispersing aluminas have enabled the development of low water demand castables. This is shown by example in Figure 6 below, where the water demand of a tabular alumina based vibration low cement castable is reduced from 6 to 3.6% by replacing an 80% alumina cement plus calcined alumina with 70% alumina cement plus reactive alumina plus dispersing alumina in the matrix fines. The hot modulus of rupture at 1500°C is increased from 5 to 23MPa without changing the chemical composition of the castable.

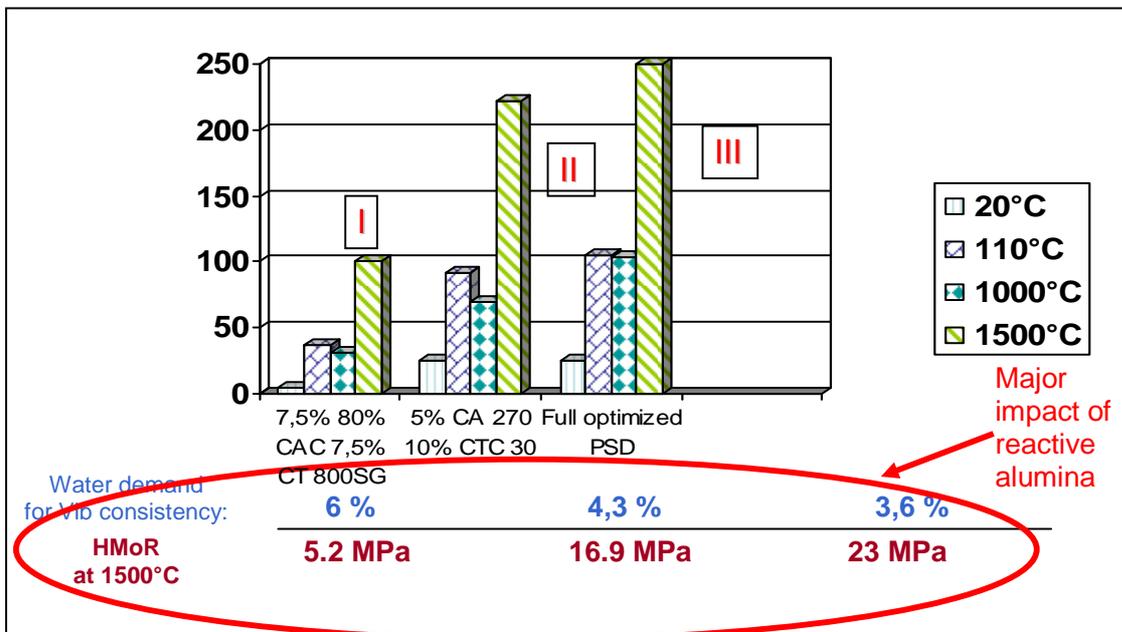


Figure 6 – Effects of Water Demand on Cold Crushing Strength and Hot Modulus of Rupture in a Tabular-Based Low Cement Vibration Castable

During the last years workability aspects have gained increasing importance because, as mentioned before, the proper installation is crucial for the performance of monolithic lining concepts. This includes the mixing behaviour of castables, the placement (vibration, self-flowing, pumping and shotcreting), and the setting (robustness against low temperatures or negative influences of castable compounds such as silica fume). Low dilatancy and an easy mixing behaviour can be a challenge especially in silica fume free castables. Special reactive aluminas have been developed for easily mixing and

pumpable castables to overcome this problem. Self-flowing castables reduce the risk of failure due to poorly densified areas of an installation.

RECENT CEMENT DEVELOPMENT

Recently, new cements have been launched to enhance the robustness of castable systems with regard to low setting temperatures or different silica fume grade quality. The approaches used are different: either additive free 70% alumina cement, where the effect is achieved by a special mineral composition of the clinker, or additive containing 80% alumina cement, where the effect is achieved by a special additive package.

In Figure 7 below, the setting time curves for tabular alumina-based ULCC with 70% alumina cement CA-14M and the new cement CA-470TI can be seen. The ULCC with the new cement CA-470TI shows a clear advantage of narrow setting time range, especially at 5°C, and avoids the phenomenon of “never setting”. Additionally, the ULCC with CA-470TI showed better flow, too.

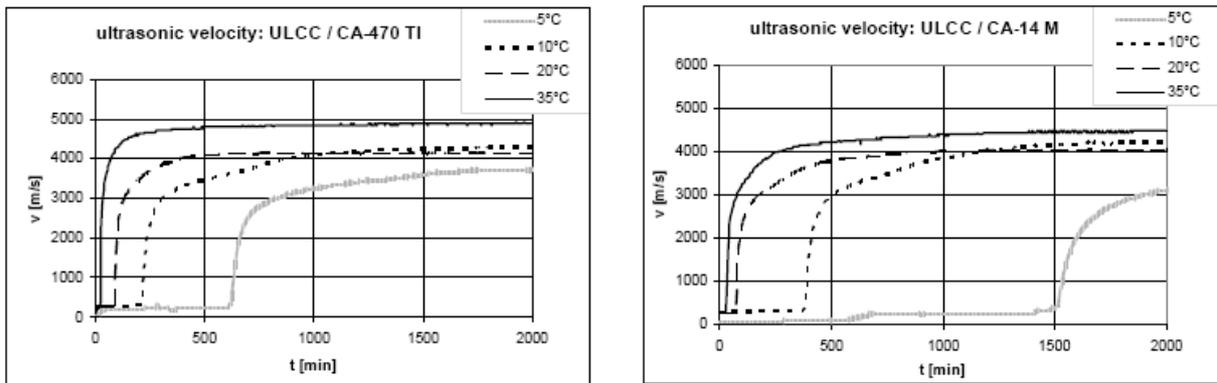


Figure 7 -.Setting time curves of ULCC with new cement CA-470TI and regular 70% Alumina Cement CA-14M

CONCLUSIONS

The various trends in refractory monolithics for steel ladles with focus on their properties and performance based on different raw materials with emphasis on advantages of highly pure synthetic discussed can be summarized as follows:

- Trend towards synthetic raw material based refractories driven by demands from modern steel making
- Coarse sized tabular alumina especially for monolithic steel ladle bottom
- Spinel containing castables for purging plugs, well blocks and nozzles
- Spinel containing combined with spinel forming for ladle side wall
- Alphabond as alternative to cement especially for silica fume containing spinel forming materials
- Reactive alumina instead of calcined alumina to boost castable performance
- Self-flow castables to reduce risk of failure for on-site casting
- CA-470 TI temperature independent cement to overcome setting problems especially at low ambient temperatures

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