Case Studies on Optimization of Selected Value-added "Premium Aluminas" to Attain a Comprehensive Leap in the Refractory Properties

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Introduction

The on-going developments in iron and steel industry for clean steel production and to secure higher productivity with better predictability made improved high alumina refractory materials an unavoidable choice. These high alumina refractories are used in abundant in the form of various castables, precast shapes, high alumina fired bricks & chemically bonded alumina-carbon bricks, slide gate plates and other functional items used in iron and steel industries. In most of the above cases, Tabular alumina based refractories outperform fused alumina (white/ brown) based refractories because of microstructural advantages and associated benefits possessed by synthetic sintered products over fused ones. Parameters like uniformity in chemical purity, homogeneity of particle size distribution and closed porosity, high toughness impart superior properties in refractories with better rheology, hot strengths, controlled expansion/ shrinkage, better thermal spalling, abrasion and corrosion resistances. However, achieving a substantial leap in refractory performance is majorly dependent, first, on the precise understanding of application's critical factors and subsequently on the role of an appropriate refractory formulation which is basically the selection (quality and quantity, both aspects) of aggregate, binder and additives among the various alternatives available.

This paper illustrates three specific cases evaluated during developmental projects with industrial partners. These three applications were considered in the areas of fired Alumina-Spinel brick, Alumina-SiC-C based ULC castable and high performing pre-cast pre-fired ladle bottom refractories, like porous plug and well block. In all these cases, the original recipe designed by the manufacturers was considered as original formulation and their properties were evaluated. Next, certain selected high-performing specialty aluminas, such as, sintered magnesia-alumina spinel AR78 grains and fines, reactive aluminas E-SY 1000 and Tabular -20 microns and combination of dispersing aluminas ADS3/ADW1 were considered to provide much needed improvements in properties of the final refractories, by utilising the typical characteristics and role of these premium aluminas to the maximum extent. The studies were carried out at ALMATIS application laboratories as well as at the industrial partners' premises and the results obtained through evaluation of critical properties are compared and translated into end application performance enhancements.

Alumina-spinel fired brick for steel ladle working lining

Original practice

Alumina-Spinel fired refractory brick for steel ladle wall lining is one of the recent innovations over last decade. The purpose of such innovation is primarily to cater the growing need of advanced metallurgy for ultralow carbon and automobile grade of steels to reduce Carbon pick-up from refractory body to liquid steel. However, in India, in absence of monolithic ladle lining as well as lower share of high quality steel production, alumina-spinel fired brick is another superior fired refractory for achieving high performance in highly corrosive metallurgical environment (such as C/S=1.5, 5% CaF_2, 2% MnO_2). With this development, the lining life has increased significantly due to much superior corrosion resistance and thermal spalling resistance compared to conventional >95% fired alumina brick or carbon bonded Magnesia-Carbon brick. Alumina-rich, pre-reacted sintered spinel AR78 has the capability to absorb FeO or MnO from corrosive slag within the free vacancies in its crystal structure. Thus slag viscosity comes down and retards slag infiltration in alumina-spinel refractories. The overall chemical purity of all ingredients including the matrix and the binder happen to be vital for such application as it was seen in the Tata (previously Corus) Steelworks in Ijmuiden, Netherlands where a fired alumina-spinel brick with 1% SiO_2 [5] achieved only 40% of the life achieved with a fired alumina-spinel brick with 0.1% SiO_2. For the end users, though the newly developed brick is targeted to lining life enhancement but also helps in reducing temperature drop in the metal bath (possible reduction in reheating % and reduction in tapping temperature) due to lower thermal conductivity of the alumina-spinel brick and also prevents odour/ fume generation of tempered Carbon bonded bricks during preheating. Thus several steel plants liked this concept and one of our industrial partner developed this brick and successfully started manufacturing and using in the steel ladle lining. The developed formulation is with Tabular alumina, calcined alumina and synthetic sintered spinel AR78.

Challenge

There was a quantum jump to 125% of previous life (in terms of heats) achieved in metal zone bricks' performance due to the change from MgO-C brick to Alumina-Spinel fired brick as per original formulation mentioned in Table1. This required further performance alignment activities of slag zone bricks and PCPF refractories in bottom lining such as well blocks and porous plugs. However, that increase in performance was not showing value addition to the user as metal zone refractories material cost increased to almost 160%. This called for some re-engineering in formulation so as to achieve tangible value addition for the end user. Our industrial partner took the challenge along with us.

Action

Series of reformulation with changes in granulometry, matrix alumina and increase of Tabular alumina share were done to get an optimized formulation listed in Table1. Further formulation change is mentioned as the modified one in Table1. The total amount of AR78 addition remained same to achieve around 5% MgO in final brick. However, major modification was planned in the size distribution of sintered spinel AR78. In case of modified formulation, finer spinel fractions are distributed in 0-0.5mm and -325 mesh sizes in place of 0.5-1mm and -325 mesh used before as well as their proportion are changed. The target was to strengthen the matrix to increase the slag corrosion resistance and enhance the thermal shock resistance. The overall particle size distribution was not disturbed as this was set to achieve optimum packing density resulting better pressed density and fired properties. In fact there was no risk of overall particle size distribution change as the individual PSD of each fractions of Tabular alumina (aggregate used) was similar to those of the sintered spinel AR78. The properties of the bricks are shown in Table2 and application of such brick is shown in Figure1.

Justification

Optimization of spinel particle size distribution showed direct impact on slag corrosion resistance. This justifies the importance of raw materials designing keeping aggregate and matrix gross weightage same. However, with the help of optimum grain size distribution of AR78 fractions with aggregate fines, a better slag penetration resistance is achieved. It is observed that finer spinel addition is more effective in resisting corrosion than coarse grain additions. However, spalling resistance was supposed to affect if right mix of coarser fraction of aggregate alumina was not supplemented in same weight% of the same fraction. This was done in proper manner and thermal shock resistance was not disturbed. Figure2 shows the improvement in spinel distribution by SEM microscopy.

Tab 1: Formulation concept followed

	Original	Modified
Synthetic HA aggregate	X	X
Calcined alumina CT9 FG	x	x
Spinel AR78 0.5-1mm	x	-
Spinel AR78 0-0.5mm	-	xx
Spinel AR78 0-0.045mm	xxx	xx

Fig. 1. Application of Alumina-Spinel fired brick in steel ladle wall (cold lining, during & after campaign)

Tab. 2: Properties of the fired bricks

Properties	Original	Modified
A.P (%)	17.5	17.3
B.D (g/cc)	3.18	3.17
CCS (MPa)	60.5	61.8
TSR at 1350°C (cycles, water quenching)	5	5
HMOR at 1400°C (kg/cm2)	11.1	11.2
PLC at 1600°C/ 5 hrs (%)	+0.08	+0.09
Slag corrosion (1650°C/ 5 hrs) (mm)	3.9	3.3

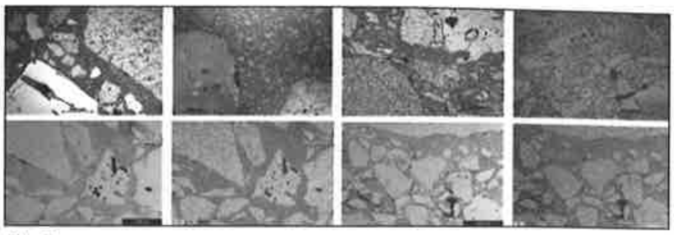

Fig. 2. SEM microstructure a cross-section from original (left) & modified (right) alumina-spinel brick

This improved alumina-spinel fired brick was lined in metal zone of 175 ton steel ladle of an integrated steel plant in India. The newly developed bricks showed further 20% improvement in lining life compared to the initial alumina-spinel brick life. Though there was some increase in the cost of refractory lining compared to traditional MgO-C linings, but the overall cost of refractory per ton of liquid steel for the steel plant has decreased due to higher life of improved alumina-spinel brick in metal zone, matching repair scheduling of other refractory items to attend their higher performance potential.

Alumina-SiC-C low cement castable for BF trough application

Original practice

In the blast furnace cast house, trough is of major importance because the hot metal and molten slag flow through it immediately after tapping. The significance of a good quality trough is not only in safely transporting the molten metal tapped from blast furnace to the torpedo or transfer ladles and allow separation of blast furnace slag by skimming but also to ensure scheduled downtime for maintenance through consistency in wear out pattern and rate and possibly to reduce the repair downtime and thereby increase metal throughput. The trough castable is subjected to erosion, slag corrosion and oxidation, FeO corrosion, abrasion and thermo-mechanical spalling caused by molten metal and slag. Al2O3-SiC-C family of ULC castable is most preferred at trough because of its high corrosion and thermal shock resistance and thermal conductivity. The major part of ULC castable constitutes of high purity alumina aggregate for refractoriness and abrasion resistance. SiC having high thermal conductivity also acts strong against abrasion, corrosion and oxidation. However, SiC inhibits sintering, therefore castable density and strength generally degrades with increasing SiC content. The slag resistance also increases significantly when the amount of SiC increases due to low wettability of SiC. Other additives are used specifically for application oriented usage such as setting or flowability in castable. The low water demand for trough castable is a desired characteristic but natures of other ingredients generally inhibit flowability and this remains a challenge. However, castables of different manufacturers generally vary in quality based on setting, flowability and consistency of wear out pattern and thus in final consumption.

Challenge

In case of ULC castable for trough application, our industrial partner was having two major issues viz. performance predictability resulting unscheduled stoppage in cast house production and uneven wear out in castable resulting excessive patching castable consumption. At the time of patching, castable setting and flowability was not favourable and thus adding to the stoppage and creating delay to restart the tapping. Thus the target was to establish better trough performance predictability by introducing balanced wear out and a much better flowability and setting in castable.

Action

It is seen that the major part of uneven wear out is caused by zonal abrasion and erosion. The role of aggregate plays a vital role here. Brown fused alumina (BFA) is one of the commonly known aggregate used, as also in this case. It is well know that the consistency of chemical impurities in different fractions of fused aggregate is very much inhomogeneous as an in-built drawback of fused alumina batch type manufacturing process. The problems aggravates in case of fines in fused aggregates. Additionally, higher impurities in BFA fines occasionally cause abnormality in castable setting and sudden erosion. Such consistency of chemical impurity is very uniform in case of Tabular due to consistency and purity in all fractions. Any type of corrosion mechanism initiates the wear-out through matrix part of the refractory body. Thus the basic modification is carried by changing the finer fractions of the aggregate from BFA to sintered Tabular alumina. Additionally, calcined alumina was removed and reactive alumina E-SY1000 is introduced as per formulation shown in Table3 to strengthen matrix and embed the aggregates stronger. This is also supposed to help in castable flowability targeted for. The figure3 explains later the quality issues in cast bars with different formulations and figure4 shows typical application of such ULC castable in blast furnace cast house.

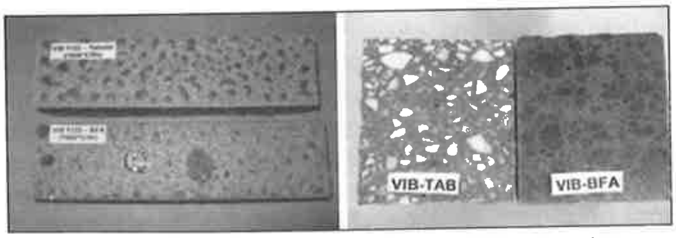

Fig.3. Lab bar casting of ULC trough castable with different formulations

Fig. 4: Application of trough castable

Tab. 3: Formulation concept followed

Figures	Original	Modified
BFA (+3mm)	20	20
BFA (-3mm)	39	19
Tabular alumina (-3mm)	0	20
SiC (2 fractions)	20	20
Calcine alumina XX	15	0
Reactive alumina E-SY 1000	0	15
70% cement CA14M	2	2
Other additives	4	4

Tab. 4: Properties of the ULC castables

	Original	Modified
Water demand (%)	6.5	4.5
VIB-flow [cm] F10	18.5	20.5
VIB-flow [cm] F30	18.0	20.2
VIB-flow [cm] F60	17.5	19.5
Density 1500°C/5 h (%)	2.89	2.81
PLC 1500°C/5h (%)	+1.1	+0.8
CCS 1500°C/5h (MPa)	68.5	79.3
CMOR 1500°C/5h (MPa)	7.3	11.4
HMOR 1400°C / 0.5h (MPa)	2.1	2.9

Justification

The change from BFA to Tabular alumina clearly reduced rate of wear. It is seen in laboratory trials that bars cast with BFA show spots (basically low melting phases) caused by local impurities and carbides entrapped in BFA fines. Such spots were not seen in Tabular containing test castable due to evenness in chemical constituents among coarse and fines (fig.3, left). Also the cut test bar with Tabular show much better embedding of grains compared to BFA (fig.3, right). The predictable wear-out pattern can also be explained from pore size distribution of BFA and Tabular alumina aggregates. The open porosity (1.05% in BFA, 1.5% in Tabular) is quite nearer whereas grain bulk density of BFA is much higher in BFA than Tabular (3.8g/cc in BFA, 3.55g/cc in Tabular) due to absence of closed porosities in BFA. This happens due to the presence of evenly distributed and small size pores in Tabular alumina (avg pore dia 0.7 micron) and works as the main reason of lower metal-slag infiltration in the modified castable compared to BFA (avg pore dia 26 micron) containing formulation (fig.5). These results in a more desirable castable density and strength and other functional properties remained unaffected. Rather a lowered mass consumption (5-6%) is found in case of the modified castable with Tabular alumina aggregate, owing to grain density difference.

The change of calcine alumina XX (d50 4.2 micron) generally used to Almatis reactive alumina E-SY1000 (d50≈1.9 micron) has multi-dimensional effects, like, better flowability with reduction in casting water demand and successive increase in hot strength due to reduced Na_2O in reactive alumina (0.08% Na_2O) compared to commonly used calcine alumina XX (0.35% Na_2O). The lower average particle size with slightly higher specific surface area of reactive alumina also increases the sinter reactivity in castable and helps in higher strengths.

The modified ULC castable has reduced unscheduled stoppages to a larger extend in actual application. Though performance benefit in terms of metal throughput was not monitored specifically but cast house was happy in the performance due to even wear out pattern and significant

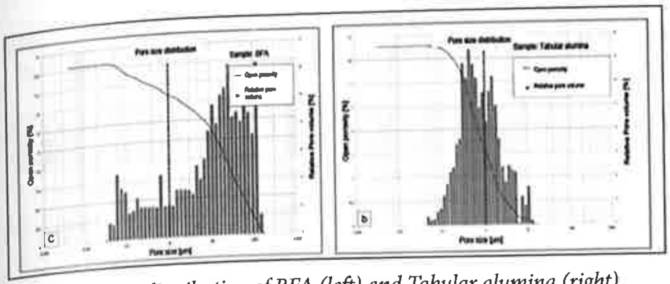

Fig. 5: Pore size distribution of BFA (left) and Tabular alumina (right)

reduction in patching castable consumption and saving of time due to reduction of numbers of patching repairs as well as absence of unwanted and unpredicted stoppages used to happen before due to uneven wear out.

Low cement castable for PCPF shapes in well block and porous plug applications

Original practice

Alumina-Spinel LC castable with Tabular alumina and sintered spinel AR78 is a proven formulation for precast and pre-fired refractory shapes in critical applications such as well block or porous plug over decades. In many similar applications such precast shapes are supplied without firing at high temperature and only after removal of chemically bonded water although it is seen that high temperature fired PCPF shape provides much reliability in critical performances. The other important application parameters like corrosion, spalling and rheological behaviour require optimum property balancing in formulation. Here Tabular alumina containing castable differs significantly from a WFA containing body due to porosity and pore distribution differences. Tabular alumina is having a characteristic microstructure of big crystals with numerous numbers of evenly distributed very small sized (<10 µm) closed pores which accounts to lower water absorption for Tabular alumina whereas WFA is having 2-3 times higher open porosity with inhomogeneously distributed large closed pores and results into higher water absorption. The WFA structure is devoid of closed pores and hence the bulk density is higher than Tabular alumina. The uniformly distributed micropores also help Tabular alumina to achieve higher thermal spalling resistance due to its ability to arrest crack propagation more effectively. Addition of different finer size fractions of sintered spinel AR78 in proper quantity improves slag corrosion resistance. For all these reasons, Tabular alumina and AR78 spinel containing LC castable is always preferred in performance stringent and highly safety prone applications like seating block, well block, porous plug, nozzles, electrode delta and other ladle pre-cast pre-fired (PCPF) units like bottom impact pad, etc.

Challenge

The original castable used to provide just sufficient heats in well block and porous plug life and these two items were the primary reasons of stoppage in maximum numbers of ladles. As ladle slag line bricks were also re-lined in same repair schedule, so the steel plant was forced to change the slag line bricks also at the same time and thus the bricks were removed at premature life having higher performance potential. The main reason of well block and porous plug change was erosion and chemical attack. It was seen that after steel tapping is finished, there was small quantity of liquid metal left at the bottom of ladle and metal was getting accumulated near well block and porous plug areas as adjacent areas were having higher height with some metal build-ups. The end user suggested to our industrial partner to find opportunities to increase wear resistance of PCPF pieces so that overall ladle life can be extended to align a balanced wear out of other repair parts like slagline bricks. The target was to increase PCPF life by 25% without affecting overall cost of full set of ladle lining.

Action

As a process of step wise improvement plan, formulations were investigated (table5). In the 1st stage (Modified-1), two different formulation concepts were introduced together viz. reducing 70% alumina cement content (targeted to improve overall high temperature properties) and introducing dispersing alumina additives (targeted to reduce water demand for castable and also to get better rheology). In 2nd stage (Modified-2), another formulation concept introduced which was the inclusion of -20 micron size fraction of Tabular alumina (targeted to have better flowability in further reduced water demand as well as increase in cold and hot strengths). An adjustment in reactive alumina CL370 content was also implemented to control possible over dosage of superfines which may lead to shrinkage after higher temperature firing. The properties of both stages are mentioned in the table.6.

Tab. 5: Formulation concept followed

	Existing	Modified 1	Modified 2
Tabular alumina T60/T64 (+1mm)	XX%	XX%	XX%
Tabular alumina T60/T64 (-1mm)	Y%	Y + 2%	Y - 4%
Tabular alumina T60/T64 (-20 micron)	Nil	Nil	R%
Spinel AR78 (0-0.5 mm & -45 micron)	Z%	Z%	Z%
Reactive alumina CL370	P%	P%	P-2%
70% cement Ca14M	Q%	Q-3%	Q-3%
Dispersing aluminas ADS3+ADW1	Nil	S%	S%

Tab. 6: Properties of the LC castables

	Existing	Modified 1	Modified 2
Casting water required (%)	7.5	5.5	4.5
VIB-flow [cm] F10	19.0	21.4	22.3
VIB-flow [cm] F30	17.5	21.0	21.9
VIB-flow [cm] F60	16.8	20.6	21.2
PLC 110°C/24h (%)	-0.08	-0.01	-0.02
PLC 1500°C/5h (%)	-0.07	-0.04	-0.03
Density 110°C/24 h (g/cc)	2.94	3.01	3.04
Density 1500°C/5 h (g/cc)	2.92	3.02	3.06
CCS 110°C/24h (N/mm2)	35.8	43.1	56.3
CCS 1500°C/5h (N/mm2)	175.0	208.5	233.1
CMOR 110°C / 24h (N/mm2)	9.9	13.4	16.2
CMOR 1500°C / 5h (N/mm2)	18.4	20.5	24.8
HMOR 1400°C / 0.5h (N/mm2)	18.6	20.8	22.3

Justification

The 1st stage modification of reduction of cement content was targeted to reduce CaO content in castable which in turn to improve the high temperature properties. In consequence, this reduces water demand to achieve proper rheology for casting and subsequently increases density and strengths and reduces porosity after firing. The introduction of dispersing alumina

ADS3 (retarder) and ADW1 (accelerator) have unique multi-dimensional advantages like better flowability at reduced water demand, control of setting time, strengthening of matrix to improve cold strength and hot properties such as hot MOR. In addition these, dispersing aluminas also provide the possibility of re-adjustment in dosage depending on setting requirement (specially required for precast items in manufacturing during particular season). With these two changes in formulation for Modified-1, the actual performance increased performance by 15% but do not met the end user final expectation.

In case of Modified-2 formulation, further reduction in casting water content took place due to presence of -20micron of Tabular alumina. The addition of Tabular alumina superfines imparts higher sinter reactivity in the body and calls for judicial quantity adjustment in matrix to avoid structural spalling arising from too dense or rigid structure. In case of this trial, this was verified in laboratory trial prior to application trial via in-direct test of hot MOR that with very low water demand like 4.5% also, the pre-fired castable bar has not achieved rigidity and is having high hot MOR. The application trial with Modified-2 formulation resulted to significant improvement in castable quality parameters (table6) and finally gave much higher performance (table7) than end user's expectation.

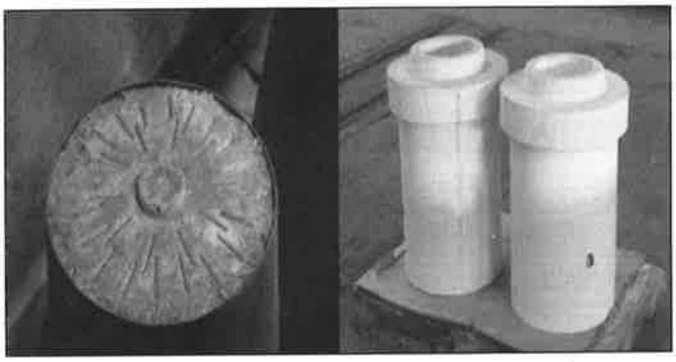

Fig. 6: Application of LC castable with Tabular alumina with AR78 spinel for critical PCPF usages

Tab. 7: Benefit in modified LC castable

	Existing	Modified 1	Modified 2
Raw materials cost	C	C + 4%	C + 6%
Impact on quality parameters	Q	Q + 10%	Q + 20%
Performance indicator	P	P + 15%	P + 35%

Conclusion

- Consistency of chemical purity in all fractions (coarse and fines) for Tabular alumina is an unique characteristics. BFA and WFA show higher impurities in fines. This is advantageous for Tabular alumina is hot properties, slag corrosion resistance and setting.
- Tabular alumina is having lower average pore size diameter and uniformly distributed closed pores compared to fused aggregates. This helps in getting higher slag-metal infiltration resistance and thermal spalling resistance.
- Rightly selected size fractions of sintered alumina-rich spinel AR 78 impart superior slag corrosion resistance. Although spinel quantity adjustment is not covered here but this remains another important criteria without mention.
- Selection of proper amount of cement governs water requirement for casting and thereby determines porosity and high temperature strengths. Reduction in cement quantity also improved high temperature properties as lime got restricted.
- Proper selection of quantity and quality of reactive alumina not only determines rheological parameters like casting water demand and flowability but also helps in sinter reactivity and thereby improve matrix strengthening which in turn provides better cold and hot properties. The application roles of CL370, Tabular -20 micron and E-SY1000 are specific and judicial selection is necessary.
- Dispersing alumina provides multi-dimensional advantages in castables and PCPF items for achieving better flowability at reduced water demand, higher cold and hot strengths and leaves possibility of dosage re-adjustment.

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