Lifetime Critical Analysis of Alumina Calciner Refractories

B. H. Teider, B. Graham, M. A. L. Braulio, J. B. Gallo, V. C. Pandolfelli

References of optimized refractory materials for lining circulating fluidized bed alumina calciners are commonly found in the literature. However, unexpected failures of these refractories are relatively usual, affecting the performance of alumina refineries in various aspects. Due to the importance of this subject, this work addresses the performance analysis of a gunning refractory that faced harsh operational conditions and resulted in a short working life. *"Post-mortem"* evaluation, *"in situ"* observation and property characterization were used to study and understand the materials' behavior in use. Based on the attained results, discussions related to a better performance potential of distinct refractories is presented, highlighting that significant improvements of calciner refractory life can still be attained having a direct benefit on the processing operational time and lost income reduction.

1 Introduction

In recent years, attention has been drawn to the objective of decreasing capital and operational costs of alumina refineries [1–4]. Some work highlighted the financial benefits of expansion projects of the processing units [5, 6] as a way to increase the production capacity and dilute operational costs without building an entire and new plant. Usually these expansion projects are carried out using the best available technology capable of increasing the process productivity, its energy efficiency and the operational availability assets.

Associated with the trend of expanding existing plants, increasing the production capacity of the equipment is also a current approach. Specifically for the calcination step, where roughly one third of the energy for alumina production is consumed [7–9], fluid-flash technology production capacity was increased from 300–500 t/d [10, 11] to units that can nowadays easily reach more than 3000 t/d [12, 13] or even 4500 t/d [14]. Although successful in reducing the specific energy consumption and decreasing specific production costs, the increasing size of calcination units also brought the need of a more controlled and stable process to avoid unplanned idle periods, which present a greater financial impact than those observed in smaller units.

Downtime causes are related to various sources, such as the equipment's design and project, the construction of the facility, operational control or maintenance [4]. Among them, it is usual to relate the refractory lining's failure as one of the main reasons of production halts. Due to the time required to cool down equipment for inspection, to demolish damaged linings, to place new linings, to dry-out and sinter the refractory, relevant repairs and overhauls represent 14 or even more days of production losses. Depending on the calciner's capacity and the economic conditions, this down time can represent a potential loss of between USD 5–15 million in revenue. Considering this aspect, the refractory working life is unquestionably a critical issue for any refinery.

Regardless of the relevance of this subject, the main evolution of calciner lining materials was mainly related to the installation speeding up processes rather than the focus on the lining's life increase. Replacing pressed bricks by plastic products is a suitable example, which is already surpassed by the use of refractory castables and pumpable mixes, either by traditional gunning or by shotcrete [15]. These latter classes of refractories are low calcium aluminate cement content bonded materials [16].

Even though conventional refractories are usually sufficient to provide a regular operation for 3 to 5 years in the most critical vessels, a rough estimate indicates that the potential gains by a twofold increase in the life time of a refractory lining (USD 5–15 million in revenue in a 6–10 years life cycle period) are relevant in a long-term evaluation, even with an occasional increase of materials and installation costs. This situation points out that the main efforts to increase the calciners' operational availability, and hence most of the financial results, must be focused on

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Fig. 1 **Evidence of thermal degradation of the refractory lining panels**

Tab. 1 **Mineralogical composition of the pristine refractory after firing for 5 h at different temperatures**

Mineralogical Composition			
Firing Temperature			
1000 °C	**1200 °C**	**1400 °C**	**1600 °C**
Corundum	Corundum	Corundum	Corundum
Mullite	Mullite	Mullite	Mullite
Traces			
Anorthite	Anorthite	Anorthite	
Gehlenite	Gehlenite		
			Vitreous
Cristobalite	Cristobalite	Cristobalite	

the technical quality of the refractory lining products rather than the decrease in the installation period, despite the known importance of the latter.

In spite of the negative impacts that refractory failures impart to the overall results of alumina refineries, which can be seen by the number of published studies relating qualitative process requirements to most suitable product properties [17–22], studies correlating *in situ* observations, *post-mortem* analyses and selection based on quantitative requirements are not easily found. Considering the unexpected behavior of a refractory material under specific conditions and the evaluation of its causes, some operational aspects, such as the maximum working temperature, were figured out. Taking this information into account, a laboratory systemic analysis was conducted and provided evidence that potential refractory alternatives could significantly increase the refractory life of that particular alumina calciner.

2 Materials and techniques

The *post-mortem* analysis was based on mineralogy changes of different layers of the used material and on the original refractory's maximum service temperature. In order to identify different constituent minerals of the refractory, the X-ray diffraction technique was carried out in *Rigaku Rotaflex RU-200B* equipment using a copper tube with nickel filter. X ray profiles were evaluated using *Brucker Difrac Plus* software.

In order to confirm the mineralogical data attained by the diffraction technique, simulations were conducted using the integrated thermodynamical database software *(FactSage®)*. The chemical composition of the refractory for the thermodynamical simulation was measured using the X-ray fluorescence technique in *PW1440 Phillips* equipment.

The products' maximum working temperature was evaluated according to the refractoriness-under-load (RUL) standard DIN 51053. In this test, cylindrical specimens (50 mm diameter and 50 mm height), previously fired at 650 °C for 5 h, were heated (5 °C/min) up to 1500 °C under a compressive load of 0,2 MPa. The materials' maximum service temperature ($T_{0,5\,\%}$) was considered to be the one at which the samples deformed 0,5 % after the initial softening temperature.

The thermal shock resistance was evaluated based on the ASTM C1171 standard and consisted of measuring the elastic modulus of the specimens [23, 24] before and after thermal cycles with holding times of 15 min at 1000 °C followed by 15 min at room temperature.

The hot modulus of rupture (HMOR) was measured according to the ASTM C583 standard, in which pre-fired specimens of each product were evaluated under the same testing temperature. For thermal stabilization, the samples were kept for 30 min at the testing temperature before measurement (loading rate of 0,750 kN/min) using *Netzsch* equipment (model 422).

3 Results and discussions

After a short time of operation, visual inspections in the calciner's combustion areas of the furnace and pre-heater vessels showed evidence that the refractory was not performing properly (Fig. 1) and resulted in an earlier and unexpected repair of the unit. Indications of refractory melting were detected during these inspections, most likely due to high operational temperatures.

Considering that using the same sort of refractory for repairing the damaged panels would result in a similar failure in the future, efforts were focused on understanding the conditions that the refractory was facing in

Chemical Composition [mass %]									
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	ZrO_2	P_2O_5
24,32	67,01	0,53	1,45	3,41	0,77	0,34	0,30	0,13	0,11

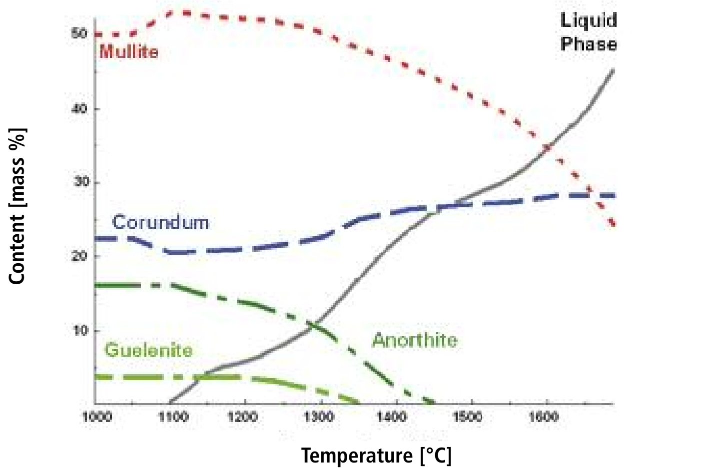

Fig. 2 **Thermodynamic simulation of the mineralogical phases with temperatures for the pristine refractory chemical composition**

order to look for more suitable refractories for this application.

Therefore, the first step of the study was to evaluate the pristine refractory's maximum working temperature. In parallel, the maximum temperature attained in service was estimated by identifying the mineralogical changes after different firing conditions. The X-ray diffraction results showed the presence of corundum (α-Al_2O_3) and mullite ($3Al_2O_3 \cdot 2SiO_2$), as the main mineral components of the used refractory bauxite aggregates. Anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) and gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) were also found and derived from a combination of the calcium aluminate cement with fine silica in the product's matrix. The cristobalite and vitreous phase in the sample pre-fired at 1600 °C, as shown in Tab. 1, was identified as a minor secondary phase.

In this study, the melting temperatures of calcium oxide containing phases were considered as fingerprints to identify at which temperatures the refractory was working within the vessels. The thermodynamic simulation (Fig. 2) showed the X-ray diffraction results, as well as a melting temperature of 1350 °C for gehlenite and 1450 °C for anorthite.

In addition to the X-ray results, which pointed out a mechanical strength loss potential at temperatures above 1350 °C, the refractoriness-under-load test indicated a maximum service temperature of 1255 °C, showing that even before the gehlenite's melting, the refractory's mechanical strength could already be spoiled. Considering the material's maximum service temperature and the working conditions, it can be stated that a critical operational situation for the refractory lining took place, which has ultimately reflected on its life time.

After evaluating the original refractory features at different temperatures, the second step of the study consisted of collecting samples from the damaged area of the furnace and pre-heater vessels for X-ray analysis. Each sample was sliced through its thickness so that identifying the distinct phases could estimate the operational temperature profile of the lining.

The first sample from the furnace vessel showed some visual aspect of degradation with an unusual surface porosity and alumina deposition in its hot face, as shown in Fig. 4.

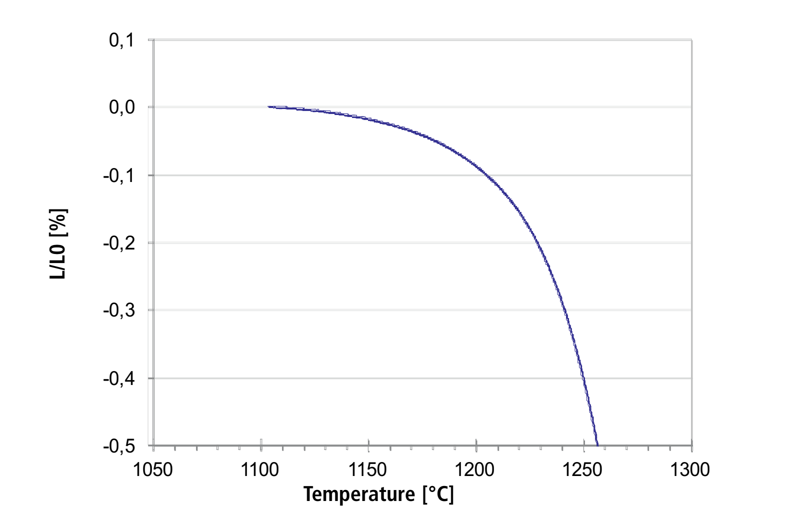

Fig. 3 **Refractoriness-under-load test of the reference refractory**

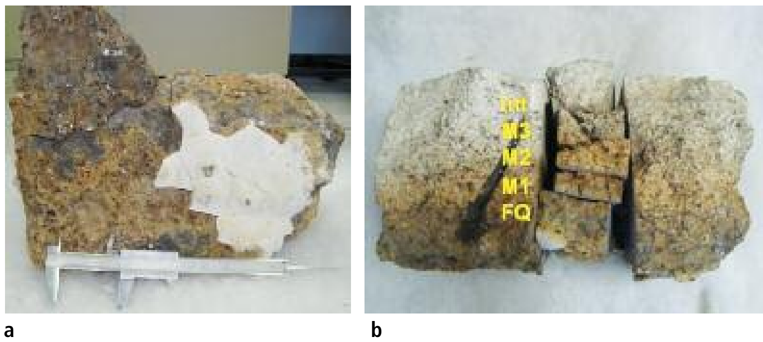

Fig. 4 a–b **Sample of the refractory material taken from the furnace vessel: (a) front view, and (b) top one**

Tab. 2 **Mineralogical composition of the original refractory in the furnace vessel**

Mineralogical Composition				
Position				
FQ	**M1**	**M2**	**M3**	**Int**
Corundum	Corundum	Corundum	Corundum	Corundum
Mullite	Mullite	Mullite	Mullite	Mullite
Traces				
Anorthite	Anorthite	Anorthite	Anorthite	Anorthite
Cristobalite	Cristobalite	Cristobalite	Cristobalite	Cristobalite

Despite the visual difference among the distinct regions of the selected sample (darker and more porous on the hot face and brighter at the back part of the sample), the phase analysis of all zones (Tab. 2), hot face (FQ), intermediate (M1, M2 and M3) and interface (Int), showed the presence of the same minerals in their composition, which firstly indicates that although it is known that temperatures may vary to some extent due to the lining's thickness, in this case all dense lining layer faced fairly similar temperatures. Secondly, the gehlenite's absence points out that the refractory operated above its maximum service temperature.

Using the original refractory's mineralogy fingerprint as a reference (Tab. 1), it is possible to point out, by combining the anorthite presence and gehlenite absence, that

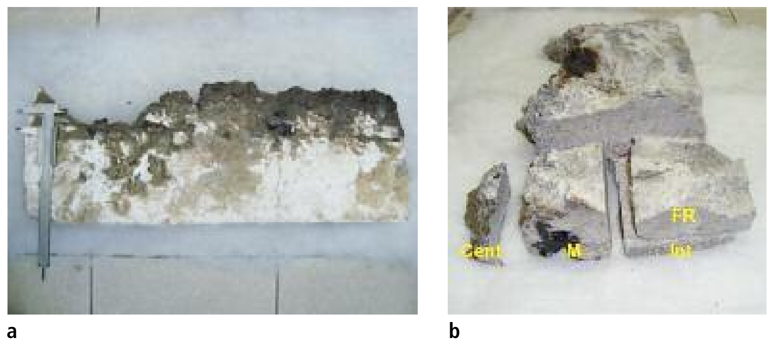

Fig. 5 **Sample of the refractory material taken from the pre-heater vessel: (a) top view, and (b) cross sectional one**

Tab. 3 **Mineralogical composition of the original refractory in the pre-heater vessel**

Mineralogical Composition			
Position (see Fig. 5b)			
Cent	**M**	**FR**	**Int**
Corundum	Corundum	Corundum	Corundum
Anorthite Vitreous	Mullite	Mullite	Mullite
Traces			
Mullite	Vitreous	Vitreous	Anorthite

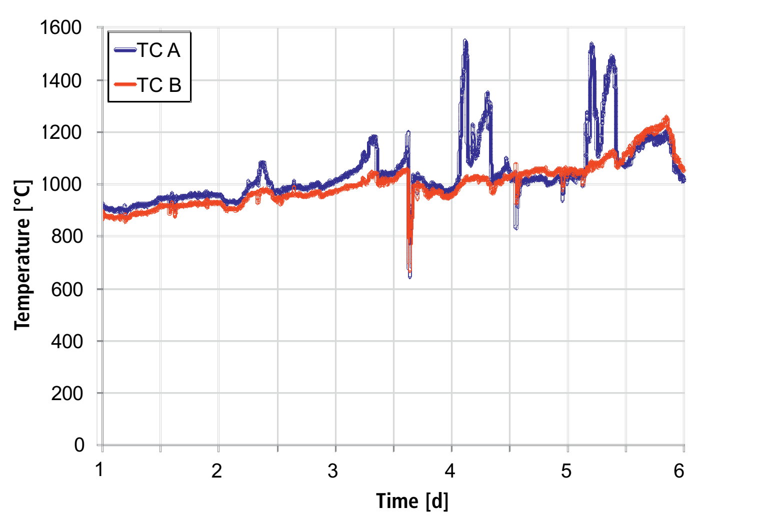

Fig. 6 **Temperature as a function of time of two thermocouples (TCA or TCB) inserted in the highest temperature areas of the unit**

the service temperatures attained at least 1350 °C, but less than 1450 °C.

The second sample, collected in the pre-heater vessel, was withdrawn from an almost fully molten panel that presented only a small remained piece of material and showed a severe degradation pattern with dark areas due to the partially burned fuel, alumina deposition in its surface and signs of vitreous phases, as shown in Fig. 5.

This refractory sample was divided into four specimens and the constituent phases were identified. Unlike the furnace's sample, the X-ray analysis (Tab. 3) showed that they did not present the same mineralogy, indicating that different service temperatures most likely took place.

The sample located at the most central area of the refractory panel (Fig. 5, Cent) showed a clearer vitreous phase than the others using quantitative X-ray analysis, which agrees with the fact that it may have faced the highest temperatures, as this region of the panel melted. However, the presence of anorthite in this sample shows that the temperature at the specimen's inner part could not have reached values much higher than 1450 °C, which was the same feature observed for the sample previously placed at the interface with the insulating refractory (Fig. 5, Int).

Unlike the central and interface samples, the intermediate (M) and hot face (FR) ones showed signs of the vitreous phase and absence of anorthite, pointing out that this area faced temperatures as high as 1600 °C, which is the second indication that the main cause of the refractory damage could have been the high temperature.

Due to these results, the need of measuring the internal air temperature in the hottest vessels was required in order to confirm whether the refractory was really being excessively exposed to high temperatures. Thermocouples were placed in some critical inspection areas and temperature peaks (Fig. 6) as high as 1550 °C during specific periods were detected, which are in tune with the mineralogical investigation.

After this analysis, it became clear that the high temperatures could be at least an important factor responsible for the short life of the original refractory and that it should be added as a criterion for the selection of an alternative material. Therefore, three further products were selected in order to evaluate their maximum service temperature. All of them were prepared using traditional gunning as the installation method. Two of the evaluated gunning mixes were classified as low cement guns, which are commonly used in alumina calciners. One is a bauxite-based (Baux-LLC-1) and the other is an andalusite-based (Andal-LLC-1) refractory. The third option was a bauxite-based gunning mix bonded with an innovative alumina compound (Baux-ABC-1). This no-calcium oxide containing product has initially been considered with a higher refractoriness potential due to the lack of gehlenite and anorthite formation. The potential for higher refractoriness is reinforced by the use of a higher alumina content matrix.

RUL tests (Fig. 7) confirmed the hypothesis of higher refractoriness for the Baux-ABC-1 product. Both the initial softening temperature and the maximum service one were higher than all low cement gun refractories, showing that it may present a better performance in the high temperature areas.

The most important feature of the hot mechanical strength results (Fig. 8) is that the Baux-ABC-1 material presented a similar strength level to the andalusite based product (Andal-LLC-1) at 1400 °C. If it is assumed that the refractoriness scales with mechanical strength at higher temperatures, this situation brings an apparent contradiction as the Baux-ABC-1 should present higher strength. Nevertheless, considering that the hot modulus of rupture (HMOR) test is under bending, it is possible to have a product with higher HMOR if it presents smaller surface defects and lower deformation resistance under compressive stresses, as in the refractoriness test, if the cohesion strength of the aggregates' bonding phase is low, which happens when a relatively large amount of liquid is present. This situation seems to be the case for the Andal-LLC-1 product.

Moreover, the thermal shock results (Fig. 9) show that even having a higher relative elastic modulus decrease after 6 cycles (39 %), the Baux-ABC-1 resulted in a more rigid structure after the thermal cycles, which within the calciner may inhibit or at least delay the panels' cracking with time and temperature.

In terms of the lining design, the higher elastic modulus results in a lower capacity to present elastic strain for a given stress. In the equipment, this sort of material will have a low capacity to absorb mechanical displacements without fracture, for instance. The fracture potential may decrease by the use of a higher number of joints to absorb the vessels' movements and avoid the panels' damage. This situation indicates that in parallel to the selection of different and high performance products, the possibility of changing the panels' sizes must also be taken into account.

After the technical characterization, it was clear that Andal-LLC-1 and Baux-ABC-1 products show a higher potential for replacing the reference material. Nevertheless, both refractories might work at their service limit in some working conditions. Because the Baux-ABC-1 product has further characteristics that provide a potential better performance of the equipment, it was selected for the future field trials.

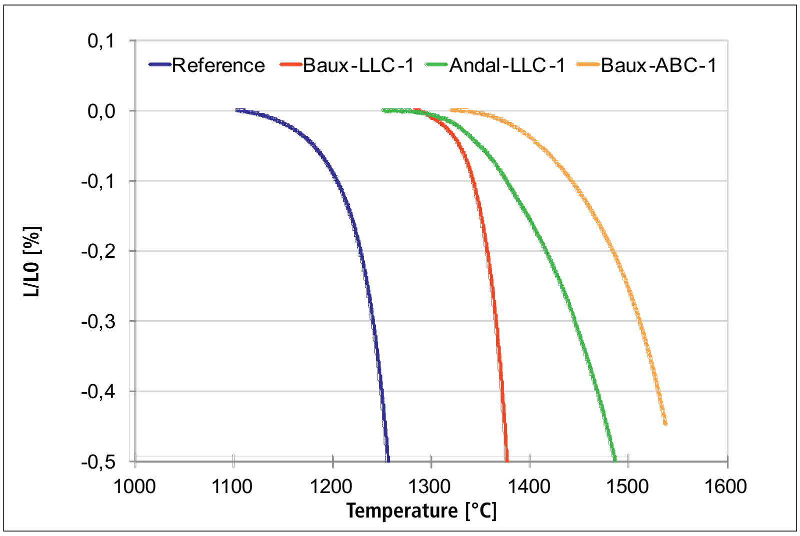

Fig. 7 Refractoriness-under-load (0,2 MPa) curves for all evaluated refractory products

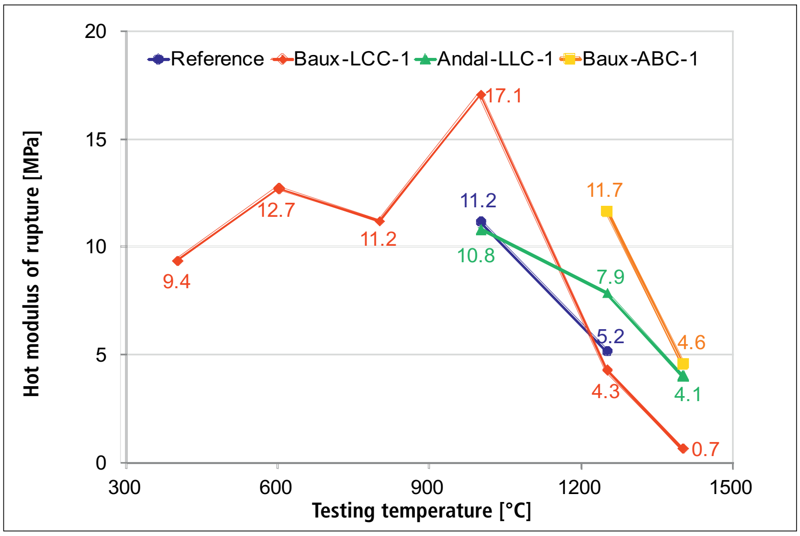

Fig. 8 Hot modulus of rupture of the evaluated products

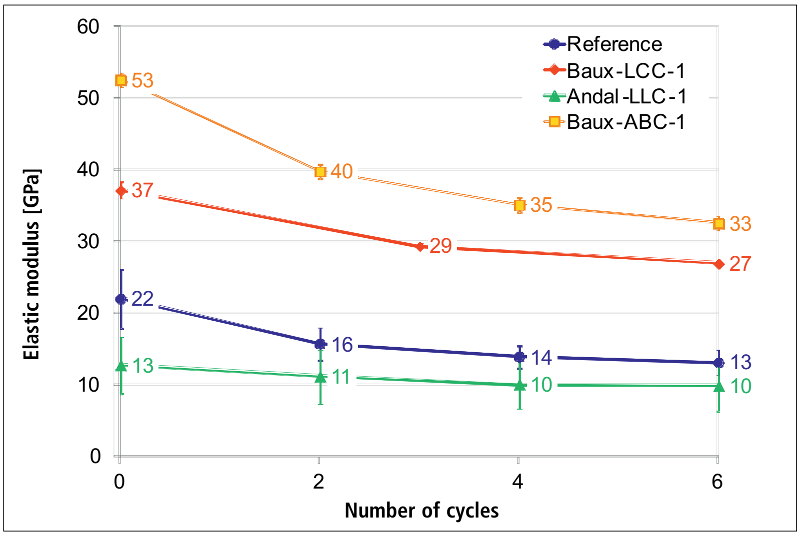

Fig. 9 Elastic modulus after thermal cycles for the evaluated products

4 Conclusions

The mineralogical evaluation of the original refractory and its refractoriness, 1255 °C, indirectly showed that the working damage that took place was a consequence of the very high operational temperatures, which were inferred to vary in the range of 1350–1600 °C and later on confirmed by the thermocouple measurements (that indicated peaks of temperatures of up to 1550 °C).

Two traditional low cement refractories and one alumina bonded gunned refractory were evaluated as potential candidates for the original lining material. The bauxite based low cement gunned refractory showed insufficient refractoriness to be applied at such high temperatures as its maximum service temperature was 1370 °C. The maximum service temperature of the andalusite based low cement gunned refractory was estimated as 1480 °C, and it was considered the best low cement refractory solution.

However, the Baux-ABC-1 composition resulted in a refractoriness of 1550 °C with satisfactory hot strength and thermal shock resistance and hence it presented the best potential to withstand these harsh service temperatures for longer periods of time. The main point learnt from this technological issue and post-mortem study is that a suitable refractory selection will only be conducted by considering the importance of a systemic overview in order to ensure its performance in such aggressive service conditions.

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