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A SPECIFIC CRITICAL ANALYSIS ON THE LIFE TIME OF ALUMINA CALCINERS REFRACTORIES

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Abstract

In the international literature it is possible to find references of optimized refractory materials for lining circulating fluidized bed alumina calciners. However, unexpected failures of these refractories are still relatively common, impacting in many ways the results of alumina refineries. Due to the importance of this subject, this work addresses the performance analysis of a refractory material which faced harsh operational conditions and resulted in a short life. *"Post-mortem"* techniques, *"in situ"* observation and properties evaluation were used to study the materials' behavior. Based on the obtained results, a discussion related to the better performance potential of distinct refractories is presented, highlighting that based on the variety of different features these materials have, significant improvements of calciner refractory life can still be attained.

Introduction

Over the past years much attention and efforts have been focused on decreasing capital and operating costs of alumina refineries [1-4]. Various works highlight the financial benefits of expansion projects [5,6] as a way to increase the production capacity and dilute operational costs without the necessity of building an entire plant from the ground. Normally these expansion projects take place through implementation of the highest available technologies capable of increasing process productivity, their energy efficiency and the assets operational availability.

Associate with the trend of expanding existing plants, the trend of increasing the production capacity of the equipments with the same objective of diluting costs is also noticeable. Specifically in the calcination step, where near one third of the energy for alumina production is consumed [7-9], the fluid-flash technology had its production capacity increased from 300-500 tons per day (tpd) since its development stage [10,11], to units that can easily reach more than 3,000 tpd [12,13], or even 4,500 tpd [14].

Although successful in minimizing specific energy consumption and decreasing specific production costs, the increasing scale 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 they used to be in smaller units.

Downtime causes are cited [4] to be related to various sources, for instance, design and project of the equipment, construction, operational control or maintenance. Among these, it is not unusual to relate the failure of the refractory lining as one of the most impacting modes of production halts. Due to the time required to cool down the equipment for inspection, demolish deficient linings, install new linings, dry-out and sintering of the refractory, significant repairs and overhauls represent 14 or more days of lost production. Depending on the capacity of the calciner and economic conditions this down time can represent the potential loss of 5-15 million dollars in revenue. Refractory life is unquestionably a critical matter for any refinery.

In spite of being the refractory's performance a constant concern, the main evolution of calciners lining materials was mainly marked by the speed up of installation processes rather than the focus on the breakthrough increase of the lining's life. The replacement of pressed bricks by plastic products is a good example, which is already surpassed by the use of refractory castables and projectable mixes, either by traditional gunning or shotcreting [15]. These latter classes of refractories using low contents of calcium aluminate cement as cold bonding agent [16].

Even though usually sufficient to sustain regular operation during 3 to 5 years in the most critical vessels, it is possible to show with a simple estimation that the potential gains by doubling the life time of a refractory lining (5-15 million in revenues in a 6-10 years life cycle period) are relevant in the long-term even with an occasional increase of materials and installation costs. This situation gives evidences that the main efforts to increase the calciners' operational availability, and hence most of the financial results, must be focused on the quality of the refractory lining products rather than the decrease of installation period, despite the known and proven importance of the latter one.

In spite of the negative impacts of refractories failures in the results of alumina refineries, attested by the number of published studies relating qualitative process requirements to most suitable products' properties [17-22], studies correlating *in loco* observations, *post-mortem* analyses and selection based on quantitative requirements are not easily found, and that is what this study intended to perform. From an unexpected response of a refractory material to specific conditions, and the study of its causes, some operational requirements were quantified. With the guidance provided by the awareness of the operational conditions, the laboratory evaluation of alternative products was customized and gave evidences that new refractory products may significantly increase the refractory life of this alumina calciner.

Materials and Methods

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

In order to confirm the mineralogical data directly obtained by the X-ray diffraction technique, thermodynamical simulations were obtained with an integrated thermodynamical database software named FactSage®, developed in a partnership of Montreal and RWTH Aachen Universities. The chemical composition of the refractory for the thermodynamical simulation was measured by X-ray fluorescence technique in a PW1440 Phillips equipment.

The products' temperature resistance was evaluated according to the refractoriness under load (RUL) standard DIN51053. In this test, previously fired specimens of 50mm diameter and 50mm height were heated (5°C/min) up to 1500°C under a compression load of 0.2MPa. The materials' maximum service temperature ($T_{0.5\%}$) was considered to be that at which the specimens deformed 0.5% after the softening temperature.

Abrasion resistance was determined as described by ASTM C704 standard by means of a "Solotest" equipment. Silicon carbide particles were projected on the surface of the specimen at an angle of 90° from the ejection nozzle using an air pressure of 53.2kPa during 450s.

The determination of the thermal shock resistance was based on ASTM C1171 and consisted of measuring the elastic modulus of the specimens [23,24] before and after thermal cycles with holding times of 15min at 1000°C followed by 15min at room temperature. This method indirectly indicates at which initiation level and propagation of cracks affected the mechanical integrity of the samples.

The hot modulus of rupture (HMOR) was measured according to ASTM C583, in which pre-fired specimens of each product are tested under the same heat treating temperature. Specimens were allowed to stabilize for 1h at the testing temperature before the determination of the HMOR (a loading rate of 0.750kN/min was used for the tests). A Netzsch equipment (model 422) was used for these measurements.

Results and Discussions

After some period of operation, visual inspections in the combustion areas of the furnace and pre-heater vessels showed evidences that the refractory was not properly responding to the service conditions (Figure 1), and resulted in an earlier repair of the unit.

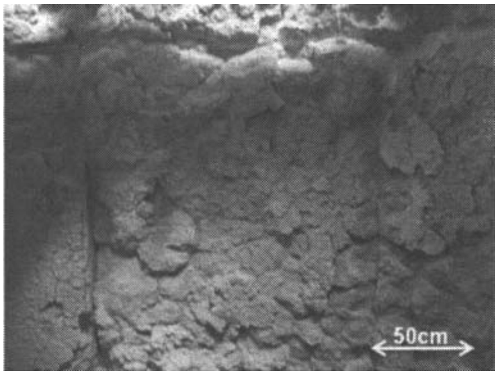


Figure 1 – Picture showing evidences of thermal degradation of refractory lining panels.

Considering that the replacement of the damaged panels by the same refractory would result in the same failure in the future, efforts were focused on the studying the conditions that the refractory was facing in order to use them in the research and selection of more suitable refractories for this application.

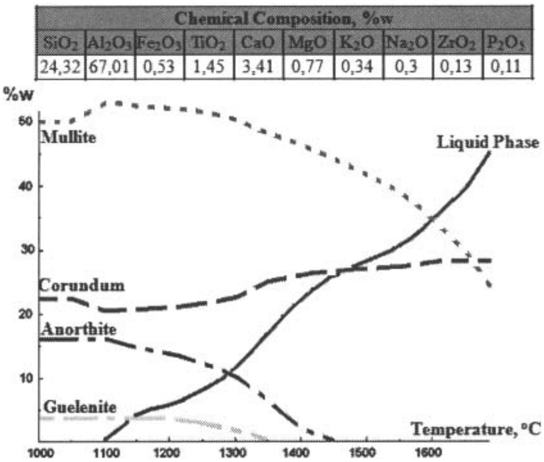
The first stage of the study was the assessment of the original refractory's temperature resistance. For that, the maximum service temperature was estimated in parallel to the identification of mineralogy changes with different firing conditions.

The X-ray diffraction results showed the presence of corundum (α-Al_2O_3) and mullite ($3Al_2O_3.2SiO_2$), of the refractory bauxite aggregates as the main mineral components, anorthite ($CaO.Al_2O_3.2SiO_2$) and gehlenite ($2CaO.Al_2O_3.SiO_2$), from the combination of the calcium aluminate cement with fine silica in the product's matrix, cristobalite as minor secondary phase and vitreous phase in the sample pre-fired at 1600°C, as shown in the Table 1.

Table 1 – Mineralogical composition of the original refractory in different firing 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	

It is important to highlight that the melting temperatures of the calcium oxide containing phases were considered fingerprints that could be used to identify at which temperatures the refractory was working within the equipment. The thermodynamical simulation confirmed the X-ray diffraction results and showed a melting temperature of 1350°C for the gehlenite phase and of 1450°C for the anorthite one.



Chemical Composition, %w									
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	0,3	0,13	0,11

Figure 2 – Simulation of mineralogical composition with increasing temperature for the original refractory chemical composition.

In parallel to the X-ray results, which pointed out a certain potential of mechanical strength loss at temperatures above 1350°C due to the gehlenite phase's melting, the refractoriness under load test estimated a maximum service temperature of 1255°C, showing that even before of the gehlenite's melting the refractory's mechanical strength could already be impaired. This is the reason why the working condition of any material above its maximum service temperature brings a critical operational situation for the refractory lining, which is ultimately reflected in its life time.

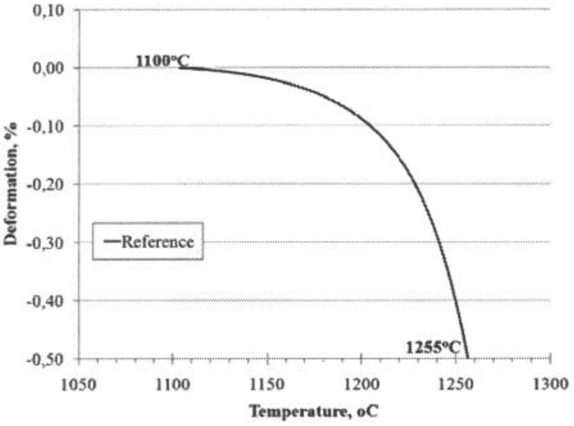
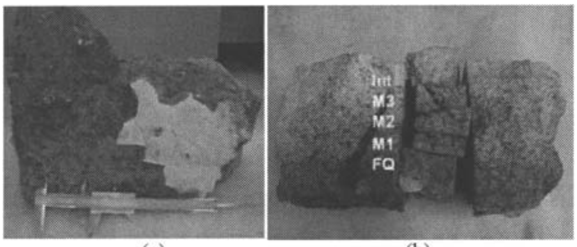


Figure 3 – Refractoriness under load test for the reference refractory.

After mapping the original refractory features with increasing temperature, the second stage of the study consisted of collecting short-life field samples from the furnace and pre-heater vessels and submitting them to the X-ray analysis. Each sample was sliced in its thickness so that the identification of distinct phases could allow the estimation of the operational temperature profile of the lining.

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



(a) (b)

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

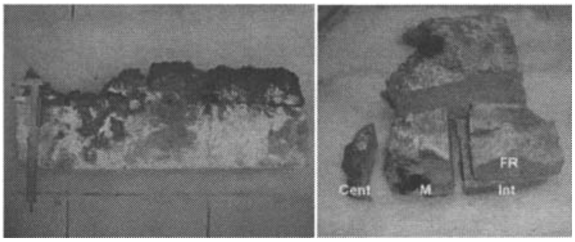
In spite of the visual difference, darker and more porous in the hot face and whiter at the back part of the sample, the phase analysis of all samples, hot face (FQ), intermediate (M1, M2 and M3) and interface (Int), showed the presence of the same minerals in their composition, which indicates firstly that although it is known that temperatures may vary in some extent as function of the lining's thickness, in this case all dense lining layer faced fairly similar temperatures. Secondly, by the gehlenite's absence, it indicates that the refractory operated above its maximum service temperature.

Table 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

Using the original refractory's mineralogy fingerprint as reference, it is possible to infer that the combination of anorthite presence and gehlenite absence evidenced that the service temperatures went up to, at least, 1350°C, however not above 1450°C.

The second sample, collected in the pre-heater vessel, was taken from an almost totally molten panel with an only small remained piece, which showed a severe degradation pattern with dark areas from the partially burned fuel, alumina sticking in its surface and signs of vitreous phases, as shown in Figure 5.



(a) (b)

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

This refractory sample was divided into four specimens and had its constituent phases identified. Differently from the furnace's sample, the X-ray analysis showed that they did not present the same mineralogy, indicating a possibility of heterogeneous service temperatures.

Table 3 –Mineralogical composition of the original refractory in the pre-heater vessel.

Mineralogical Composition			
Position			
Cen	M	FR	Int
Corundum	Corundum	Corundum	Corundum
Anorthite Vitreous	Mullite	Mullite	Mullite
Traces			
Mullite	Vitreous	Vitreous	Anorthite

The sample placed in the most central area of the refractory panel (Cent) showed a more evident vitreous phase pattern than the other samples, which agrees with the fact that it may have faced the highest temperatures, since the central part 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 from the sample previously positioned at the interface with the insulating refractory (Int).

Differently from the central and interface samples, the intermediate (M) and hot face (FR) ones showed some content of vitreous phase and total absence of anorthite, which indicates that this area faced temperatures at least close to 1600°C, which brings the second indication that the main cause of its short-life could have been the excessive temperature.

This investigation brought the necessity of measuring the internal air temperature in the hottest vessels in order to check whether the refractory was really being excessively exposed to high temperatures. Thermocouples were installed in some areas and it was possible to observe temperature peaks as high as 1550°C during specific periods, which confirms the mineralogy investigation.

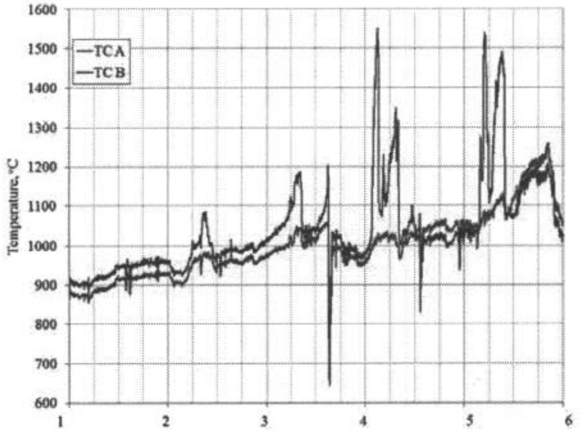


Figure 6 – Temperature over time in days for two thermocouples inserted in the highest temperature areas of the unit.

At this moment 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 must be included as a criterion for the selection of an alternative refractory.

Three alternative products were chosen to be technically evaluated. All of them used traditional gunning as installation method. Two of the evaluated gunning mixes were classified as low cement guns, which are common 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, cold 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.

Results of the refractoriness under load confirmed the hypothesis of higher refractoriness of the Baux-ABC-1 product. Both the softening temperature and the maximum service one ended up higher than all low cement gun refractories, representing an evidence that it may present a better performance in the high temperature areas.

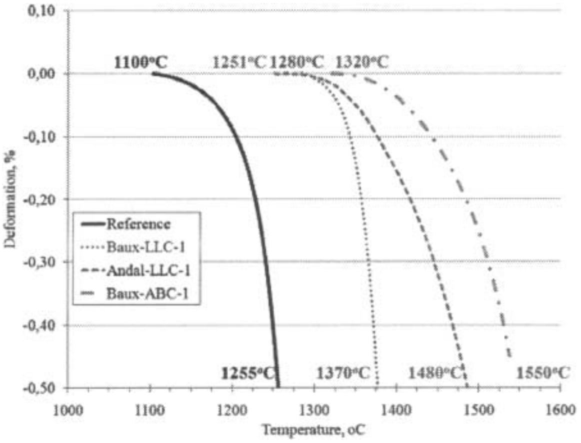


Figure 7 – Refractoriness under load test for all evaluated refractory products.

The most impacting feature of the hot strength results is that the Baux-ABC-1 material presented similar strength to the andalusite based product at 1400°C, with indications that they may invert positions at higher temperatures. If it is assumed that the refractoriness scales with mechanical strength at higher temperatures, this situation brings an apparent contradiction with the refractoriness test, in which the Baux-ABC-1 should present higher strength.

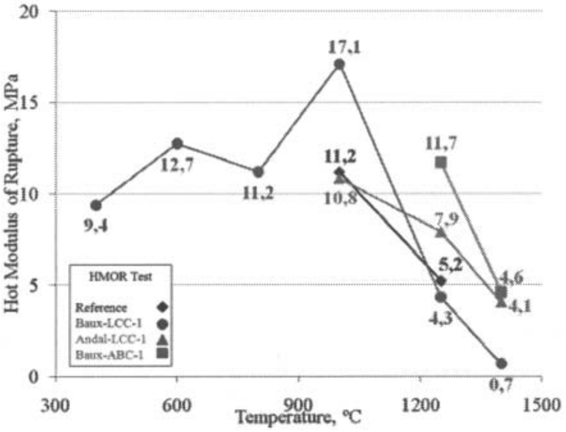


Figure 8 – Hot modulus of rupture and room temperature abrasion resistance of the evaluated products.

Nevertheless, if it is considered that the hot modulus of rupture test is a bending one, it is possible to have a product with higher HMOR if it presents smaller surface defects, and lower deformation resistance by compressive stresses, as in the refractoriness test, if the cohesion strength of the aggregates' bonding phase is decreased, 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 show that even with higher relative elastic modulus decrease, the Baux-LLC-1 resulted in a more rigid structure after the thermal cycles, which within the calciner may inhibit or at least delay the panels' deformation with time and temperature.

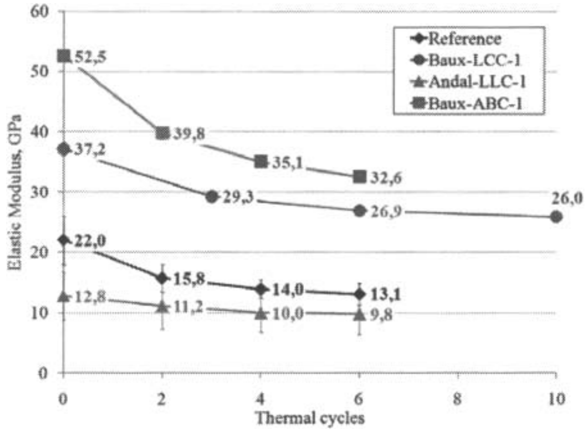


Figure 9 – Elastic modulus after thermal cycles for the evaluated products.

In terms of the lining design, the higher elastic modulus results in a lower capacity to present elastic strain for a given stress. Within the equipment, this sort of material will have low capacity to absorb mechanical displacements without fracture, for instance. The fracture potential may be 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 simple replacement of any product, the possibility of adjustments in panels' sizes must be analyzed.

After the discussion of all results, it was relatively clear that the Andal-LLC-1 and Baux-ABC-1 products are the main potential alternatives for the reference material, despite not presenting a safety factor in the maximum service temperature, since both will work at their service limit in some occasions. However, since the Baux-ABC-1 product has further characteristics that provide a potential better performance of the equipment, it was selected for the field trials.

Conclusions

The mineralogy of the original refractory and its refractoriness, 1255°C, showed indirectly that the short-life occurred due to service at excessive operational temperatures, which were indirectly inferred to stay between 1350°C-1600°C and directly confirmed by the thermocouples that measured temperatures up to 1550°C.

Two traditional low cement refractories and one alumina bonded gunned refractory were evaluated as potential replacements for the original lining material. The bauxite based low cement gunned refractory showed insufficient temperature refractoriness to be applied at such high temperatures as its maximum service temperature was estimated as 1370°C. The andalusite based low cement gunned refractory had its maximum service temperature estimated as 1480°C, and it was considered in the best low cement evaluated option. However, the latter one resulted in a refractoriness of 1550°C with satisfactory hot strength and thermal shock resistance and hence it was considered the best potential to withstand the service temperatures for the longer periods.

Acknowledgements

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