POST MORTEM ANALYSIS OF THE FLUE WALL BRICKS USED IN ANODE BAKING FURNACES

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ABSTRACT

The advances in the aluminum industry and the high competitiveness among the companies promoted the choice for Pre-baked technology in electrolytic cells. One of the main challenges of this system is the maintenance cost reduction of the refractories used in anode baking furnaces. In the latest years, improvements were carried out in anode firing process and in high chemical resistance refractories development. However, the bricks' corrosion can still be quoted as the main parameter used by the aluminum producers in order to evaluate its replacement. Therefore, the present work aims to present a case study of high chemical attack in the flue wall bricks which resulted in their replacement and a major increase of the anode furnace maintenance costs. The results showed that the materials chemical attack increase was related to a change in the furnace process. Additionally, it was pointed out that the quality control of the green anode, the recovering coke and the refractories compositions is essential, when the bricks corrosion reduction is aimed.

Key-words: aluminum, refractory, anode

1. Introduction

The great number of aluminum producers and the current worldwide economic crisis forced the companies to adopt strategies of reducing the energy consumption and lowering the metal production costs [1]. Considering the pre-baked technology plants, the anode baking furnaces became an important issue due to the high expenses with refractory materials, operational practices and fuel.

Basically, these furnaces are comprised by dense refractories, named flue wall and tie bricks, and insulating refractories which are the thermal barriers in order to keep the heat and save the energy. Thus, the refractories materials, mainly, the flue wall brick plays a main role in the process, as its selection and performance have a major impact on the furnace construction and the maintenance costs. Additionally, the demand for higher anode productivity through a shorter firing cycle also stimulates the search for high quality materials [2-3].

The practical experiences show the importance of a suitable selection of these refractories due to high maintenance costs of the furnace and the close correlation between the bricks properties and the baked carbon block quality. However, besides the refractories quality, others parameters clearly affect the materials working life along the carbon block heat treatment: operational practices such as loading and unloading of the anodes, baking temperature range, furnace design and chemical environment [4]. Among these factors, the materials corrosion, which is mainly related to the furnace environment, can be quoted as the main variable used by the aluminum producers to replace a used brick [5].

In this sense, the present work aims to present a case study of high corrosion in the flue wall brick used in anode baking furnaces. The materials working life was reduced by half due to a high chemical attack and this increased the furnace maintenance cost. In order to understand the main reasons that can lead to an earlier brick's replacement, a systemic analysis based on the information's from the literature and the furnace operational practices, was carried out. As a result, two hypotheses were formulated:

Hypothesis 1: Brick's physical properties - This approach aims to verify whether a brick quality change was carried out by the refractory suppliers which could have affected the materials' chemical attack resistance. This is an important feature because, along the time, for different batch of brick's supply, a change in the flue wall bricks chemical composition or in their firing conditions could affect the phases present in the brick's microstructure, increasing the permeability and porosity of the materials, speeding up the bricks' corrosion.

Hypothesis 2: Anode furnace environment – Increase the harmful elements (alkalis, iron oxide, sulfur, fluorine and carbon monoxide [4]) concentration present in the furnace can also speed up the corrosion reactions, even if the bricks present a high chemical attack resistance. Therefore, a post mortem analysis of the used bricks was carried out in order to evaluate the brick's corrosion behavior. Additionally, an evaluation considering the baking process, the green anode and the recovering coke compositions, was evaluated in order to investigate the impact of theses raw materials in the brick's corrosion intensity.

2. Methodology

Hypothesis 1:

In order to check if the as received brick used in the anode furnace plant did not change its composition from the batch to batch, some tests were carried out, such as apparent porosity, apparent density, permeability and chemical analysis and the results were compared with the values obtained at the qualifying step [6]. It is important to highlight that the evaluated properties were performed with as received bricks of different batches from the same supplier.

The evaluation of the apparent porosity and density was based on ASTM C830.

The air permeability at room temperature was evaluated using an internal standard procedure based on ASTM C577, using with 70 mm diameter x 25 mm thick cylindrical samples. The pressure drop and the air velocity were measured and the permeability constants were based on Forchheimer Equation [7].

The chemical analysis was performed according to NBR 3198. For each composition, 200 grams were prepared by a milling in a tungsten carbide shatter box and the analyses performed in florescence X-ray equipment (PW 1440 model from Phillips).

Hypothesis 2:

In order to verify the bricks corrosion degree the post-mortem analysis of the flue wall bricks was performed. From the same furnace, three used bricks from distinct regions and all with 83 working life cycles were analyzed. From each used brick, 3 samples were withdrawn, using a Clipper equipment. It is important to highlight that the letter “A” is related to the anode side of the bricks, “B” stands to the middle area and “C” to the burner side. The chemical analysis was used to analyze the brick’s microstructure corrosion.

3. Results and Discussions

3.1 Brick’s physical properties

Comparing the physical properties results of the present brick and those obtained in the qualifying step, it is possible to observe that the refractory supplier did not change the brick’s quality. This can be attested by the values of porosity, density and permeability which, practically, kept the original results (table I). Additionally, the table II gives a strong indicative that the flue wall brick holds the same chemical composition along the time. The alumina and silica content remained constant, about 50% in weight and the low content of alkalis, sulfur and iron oxides and fluorine were observed for both data. Moreover, the absence of carbon and sulfur in the as received brick composition and their presence in the post mortem analysis is a clear indicative that the source of each element inside the furnace must be investigated.

Therefore, if, along the time, an increase of the chemical attack in the bricks was detected by the aluminum producer, most likely this can not be related to the flue wall brick’s properties and the second hypothesis must be checked.

Table I: Flue wall bricks physical properties from qualifying up to the present.

	Porosity (%)	Density (g/cm^3)	k_1 (m^2)	k_2 (m)
Qualifying	14.00 ± 0.60	2.41 ± 0.01	2.43 E-13	1.87 E-08
Present	12.17 ± 0.32	2.46 ± 0.01	7.13 E-13	3.87 E-08

Table II: As received flue wall bricks chemical composition.

	Loss on Ignition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	SO_3
Qualifying	0.09	46.73	48.85	1.39	2.32	0.15	0.02	-
Present	0.08	46.67	49.11	1.28	2.23	0.13	0.03	0.01

3.2 Post Mortem Analysis of the used bricks.

3.2.1 Chemical analysis

In order to analyze the bricks' corrosion level, the chemical analysis was performed. The literature shows that five main elements react with the refractories microstructure, reducing the material's working life: alkalis, iron oxide, sulfur, fluorine and carbon monoxide [4].

ALKALIS

Table III shows the profiles of to the alkalis (sodium and potassium oxides) content on used samples and as received one. Thus, four distinct behaviors were observed: the as received brick presented the lowest and constant values of alkalis along its cross section; sample 1 presented a high concentration of alkalis at the anode side and at the middle of the brick, with lower values at the burner side. Very likely, the alkalis gases permeated the pores of the bricks and reacted with the microstructure, resulting new expansive phases such as kaliophilite and nepheline which can damage the materials' structure (equation 1 and 2) [8-10]. Additionally, according to these reactions, a carbon deposition is verified in the bricks pores which generates stresses in the materials. After the attack, the alkalis filled in the bricks pores and acted as a barrier to the gas penetration, reducing the alkali content at the burner side. It is important to highlight that this is just a hypothesis.

Sample 2 presented a distinct behavior when compared to the other used bricks: a high concentration of alkalis all trough the brick. Most likely, this occurred due to the high chemical attack at high temperatures and this can be related to the brick position inside the furnace.

Sample 3 presented a similar behavior to sample 1 with high alkali content at the middle and at the burner side of the brick. However, at the anode side, the alkali content was close to the as-received brick. No clear reason was found to explain this behavior.

$$2Na_{2(g)} + \frac{2}{3}(3Al_2O_3 \cdot 2SiO_2)_{(s)} + \frac{8}{3}SiO_{2(l)} + CO_{(g)} \rightarrow 2\underbrace{(Na_2O \cdot Al_2O_3 \cdot 4SiO_2)}_{\text{Nepheline } (\alpha = 16.9 \cdot 10^{-6}\ {}^{o}C^{-1})}{}_{(s)} + 2C_{(s)} \quad (1)$$

$$2K_{2(g)} + \frac{2}{3}(3Al_2O_3 \cdot 2SiO_2)_{(s)} + \frac{8}{3}SiO_{2(l)} + CO_{(g)} \rightarrow 2\underbrace{(K_2O \cdot Al_2O_3 \cdot 4SiO_2)}_{\text{Kaliophilite } (\alpha = 8.5\text{-}11.5 \cdot 10^{-6}\ {}^{o}C^{-1})}{}_{(s)} + 2C_{(s)} \quad (2)$$

IRON OXIDE

According to table III, all used bricks presented a homogeneous behavior: the iron oxide content was reduced from the burner side till the anode one. Most likely, the iron oxide was reduced, generating metallic iron that can react with the carbon monoxide present in the system (equation 3 and 4) [11-14]. As final product of this reaction, the carbon will be formed into the pores of the bricks, damaging the materials. If the flue wall brick is the main responsible to add this harmful compound in the system, the aluminum producer must search for compositions with lower iron oxide content in order to avoid more carbon deposition in the bricks.

$$3C_{(s)} + Fe_2O_{3(s)} \rightarrow 3CO_{(g)} + 2Fe_{(s)} \qquad T > 300^{o}C \qquad (3)$$

$$3Fe_{(s)} + 2CO_{(g)} \rightarrow Fe_3C_{(s)} + CO_{2(g)} \qquad 400^{o}C < T < 800^{o}C \qquad (4)$$

$$\downarrow$$

$$Fe_3C \rightarrow 3Fe_{(s)} + C_{(s)}$$

SULFUR

All used samples presented an increase on the sulfur content, mainly, on the anode side (table IV). Comparing these results with those observed in the table II, it is possible to point out that the sulfur origin can not be related to the brick's composition. Hence, the source of this element inside the furnace must be investigated. Additionally, at high temperatures, this available sulfur present in the material is oxidized, resulting SO_x. This oxide can combine with the water vapor from the atmosphere, resulting sulfuric acid which can spoil the materials properties at the working conditions [11].

FLUORINES

Table IV shows an interesting behavior of the bricks, as the silica content of two used samples was reduced just on the anode side of the bricks. Most likely, a reaction between fluorine and silica occurred, generating $SiF_{4\,(g)}$. At high temperatures, this gas is released out of the brick, creating micro cracks and voids [11]. However, the silica content of sample 2 presented an increase on the anode side. As presented previously, the chemical attack of this brick was intense along the furnace operation, leading to a non-expected behavior.

CARBON MONOXIDE

In a reducing atmosphere as observed on anode baking furnaces, the carbon from the recovering coke and the green anodes reacts with the oxygen from the system, generating carbon monoxide which can be dissociated in carbon dioxide and solid carbon. This reaction is known as “Boudouard Equation” (equation 5).

Sample 3, mainly, presented a thick layer of coke impregnated on the anode side and the highest value of carbon content (table V). It is important to highlight that this behavior is not desired because it reduces the pit size and increases the furnace operational costs due to the materials cleaning process or their replacements.

$$2CO_{(g)} \rightarrow CO_{2(g)} + C_{(s)} \tag{5}$$

Table III: Alkali and iron oxide content in the flue wall bricks.

(wt%)	Alkalis			Iron Oxide		
	A	B	C	A	B	C
As received	0.16	0.16	0.16	3.51	3.51	3.51
Sample 1	0.83	0.90	0.32	3.40	3.37	3.47
Sample 2	0.76	0.67	0.68	3.16	3.32	3.22
Sample 3	0.20	0.79	0.27	3.47	3.42	3.47

Table IV: Sulfur and Silica content in the flue wall bricks.

(wt%)	Sulfur			Silica		
	A	B	C	A	B	C
As received	0.01	0.01	0.01	46.67	46.67	46.67
Sample 1	0.32	0.03	0.01	44.55	46.19	46.05
Sample 2	0.09	0.08	0.04	49.49	46.92	49.05
Sample 3	1.26	0.19	0.05	45.60	47.05	49.15

Table V: Carbon content in the flue wall bricks.

(wt%)	A	B	C
As received	0.08	0.08	0.08
Sample 1	5.43	0.15	0.12
Sample 2	0.91	0.57	0.17
Sample 3	17.04	1.33	0.16

The post mortem analysis attested that the brick's failure was mainly related to the presence of several harmful elements that resulted an intense chemical attack. Additionally, it is important to highlight that the bricks corrosion behavior were not similar and, most likely, the bricks' position inside the furnace influences the materials corrosion level. Thus, the next step of this study is to identify the origin of each harmful component in the furnace in order to reduce their contents and, consequently, decrease the materials corrosion.

During the carbon block heat treatment, other two raw materials present in the furnace can be responsible to supply the harmful components to the bricks: the green anode and the recovering coke. Hence, an investigation about their compositions, along the time, was performed in order to verify the interaction between the brick's corrosion intensity and the chemical composition of these raw materials.

GREEN ANODE

Table VI shows two different situations occurring in the furnace simultaneously:

- since 2003, the green anode, which contains pitch, green coke and recycled anode (butts), has its butts content reduced. As the recycled anode is the main source of sodium and potassium oxides, it seems that the furnace environment has been less damage to the materials, affecting positively the bricks performance.
- the sodium content in the butts was also reduced with the time. Hence, there was an improve of the recycled anode cleaning operation, which reduced the sodium content in the furnace environment.

Nevertheless, according to table VII, the difference between the sodium content in the green anode and the baked one, increased in 2003. Therefore, the alkali content available inside the system to react with the brick had a pronounced increased in this year, resulting in a high chemical attack and, consequently, a reduction in the materials' working life. Additionally, it is important to highlight that a time-to-time chemical control of the green anode is essential to follow the brick's performance.

Table VI: Butts and Na content in the green anode.

	2002	2003	2004	2005	2006	2007
Butts in anode mix (%)	24.90	27.20	24.33	20.56	20.65	18.00
Na in butts (ppm)	4315	3665	4578	2869	2294	2548

Table VII: Sodium content in the green and baked anode.

	2002	2003	2004	2005	2006	2007
Na content in green anode (ppm)	429	582	638	543	633	634
Na content in baked anode (ppm)	412	298	516	421	476	422
Difference (ppm)	17	284	122	122	157	212

RECOVERING COKE

The recovering coke also has an important influence in the materials performance. According to table VIII, the sulfur present in the furnace is mainly related to the recovering coke. Additionally, a new element in the system was detected: vanadium. The alkalis combined with vanadium results in low melting phases, reducing the brick's refractoriness [11]. Hence, the recovering coke must also be chemically controlled in order to decrease the brick's damage.

Table VIII: Recovering coke composition.

(wt%)	Iron	Vanadium	Sulfur	Silicon	Ash
Recovering Coke	0.0022	0.135	5.1	0.0018	0.5

4. Conclusions

Comparing the data obtained for the material supplied in qualifying and the present one, no change in the brick's composition was observed. Therefore, the shorter brick's working life was not related to the flue wall brick's quality. In this sense, a suggestion for the aluminum plants is to perform periodical quality control tests for as received brick in order to guarantee that they did not change for different bricks supplier delivery. Usually, the data-sheet lasts much longer without changes than the actual compositions.

The post mortem analysis confirmed severe corrosion in the bricks. Hence, in order to increase the flue wall brick's working life, the aluminum producer must also reduce the concentration of the harmful elements in the furnace environment through a time-to-time chemical quality control of the green anode raw materials and the recovering coke. Additionally, the search for bricks with low alkali, free silica and alumina should be kept always in progress.

The analyses pointed out that something occurred in the furnace in 2003 that could have sped up the flue wall bricks corrosion. This hypothesis was confirmed by the aluminum company, as at that year, a high amount of green anodes were bought from another anode paste plant which enhanced the concentration of the harmful elements inside the furnace and, consequently, the anode furnace maintenance costs increased due to the flue wall brick's working life reduction.

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6. References

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