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Cathode performance evaluation at Votorantim Metais – CBA

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Abstract

The cathode is a set of items with a high cost in the primary aluminum production, this set is usually composed of carbon materials, refractory and insulating materials, which have their basic raw materials extracted from nature. There is great concern about cathode performance, this with respect to cathode life and energy efficiency, several works have been performed in order to maximize the cathode life thereby avoiding costs and waste, more commonly known as SPL (spent pot lining) as well as an hazardous waste to the environment and has a high cost for recycling.

In this paper, the main findings extracted from pot autopsies will be presented as an important methodology to maximize cathode life at Votorantim Metais (CBA).

Introduction

The cathode life has been widely studied over the years. Grjotheim [1] summarized the main aspects that have an impact on cathode performance (table 1):

Table 1. Key-parameters aspects for pot life performance.

Cathode life		
Design / assembly	**Operation**	**Materials quality**
Precision to assembly	Thermal balance	Chemistry composition
Cathode and side wall design	Bath composition	Cathode block homogeneity
Pot sealing to avoid air oxidation	Work temperature	Mechanical and electric properties./Abrasion resistance
Mechanical stability of the shell	Current distribution	Dilatometric properties
Electromagnetic compensation	Sludge	Resistivity towards tension and stresses caused by alkali intercalation
Bus bar design	Start-Up	Stability towards structural changes (graphitization).

The degradation of the cathode is a result of several factors that work together, as chemistry wear, mechanical stress and electrochemistry wear.

The main chemical reaction which has impact on cathode life occurs in specific regions of the pot such as carbon/Al and carbon/bath/Al. This reaction produces aluminum carbide (Al_4C_3) that accelerates the process of cathode erosion due the high wear potential of this particle. The Al_4C_3 occurs by an electrochemical [4] reaction as follow:

$$4Al_{(l)} \leftrightarrow 4Al^{+3} + 12e \qquad (1)$$

$$4Al^{+3} + 12e^{-} + 3C \leftrightarrow Al_4C_3 \qquad (2)$$

This phenomena (equation 2) is influenced by high current density, disordered carbon structure. As a result, voids are created, increasing the erosion path [4] and the possibilities to shorten the potlife.

Lining materials such as barrier bricks and insulation bricks are affected by chemical reaction with sodium which promotes a "Sodium swelling". Harris and Oprea [2] have described the mechanism of the Sodium swelling as a volumetric expansion caused by a formation of a new phase which promotes an expansion around 20%. The Al_2O_3/SiO_2 factor, pore geometry and permeability of the brick could imply on sodium penetration rate which promote an accelerated degradation of the lining materials.

A poorpre-heating before a pot start-up can promote cracks and strains on the lining materials and in the cathode blocks. The start-up procedures should be smooth and well controlled to avoid a premature pot shut down. The side lining material such as ramming paste have to be well-tamped to avoid excessive shrinkage and formation of layers. The baking process of these materials should be done according to suppliers recommendation. A dilatometric curve should be considered to set the pre-heating curve.

The cathode average life at VM-CBA is presented in Figure 1. This increase on average life is related to gradually change of the cathode from semi-graphitic to graphitic blocks also the whole lining materials was changed. These modifications were necessary to allow pots to operate at higher load (from 115kA to 130kA). At this moment, potlines are operating closer to the final target, in a range of 125 to 128kA.

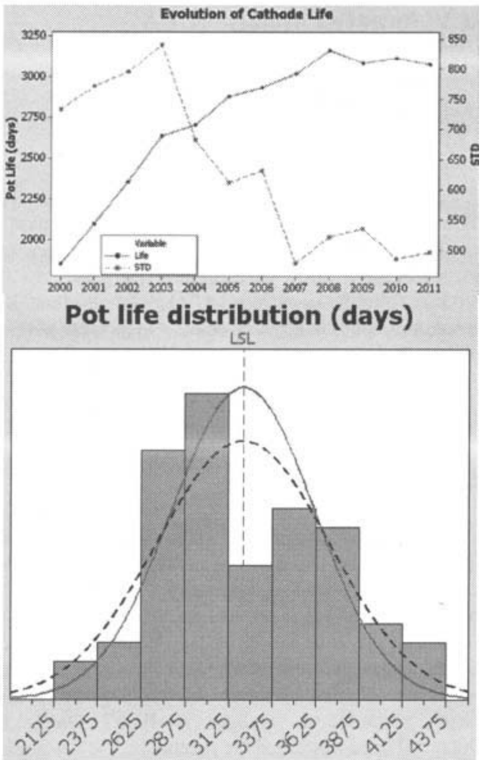


Figure 1. Cathode life evolution and its distribution

The pot life average in 2010 was 3210 days and the main reason for the shutdown was Iron contamination and the high energy consumption due the increase of the cathode voltage drop (CVD).

According to Figure 1 about 50% of pot life is lower than the 3210 days, it implies in production losses and increase in costs.

Some autopsies were performed to identify the reason for an early failure and also to check the aspects of lining materials and arrive at conclusions concerning why something went wrong and to make decisions aiming to increase potlife.

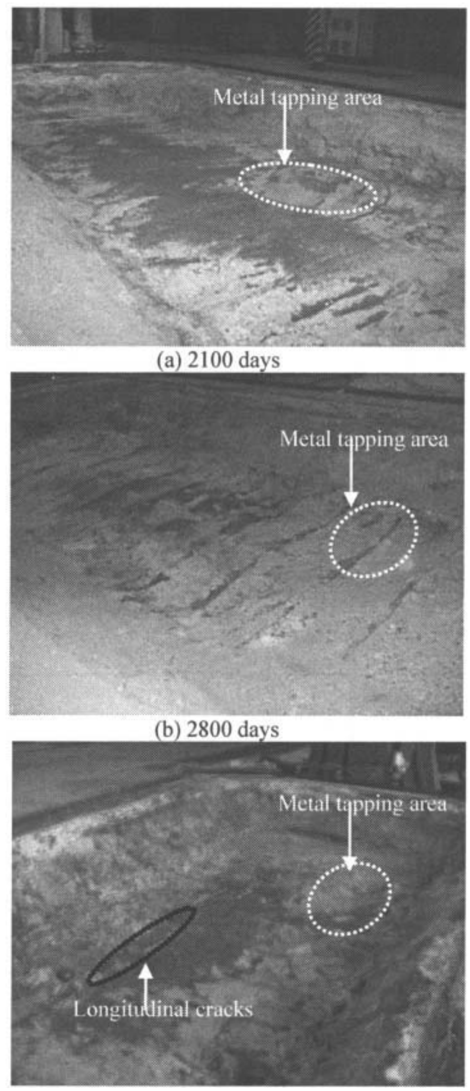
Autopsies

Autopsies in general is carried out to identify the reason of early failure of pot or even to evaluate if some specific changes on the lining materials or cathode blocks are appropriate. Cathode autopsies at VM-CBA were performed to identify the main mechanism of failures and understand what changes are necessary to extend the potlife.

The autopsies were made following the procedure described bellow:

- Cleaning of cathode surface – to remove bath, sludge and aluminum;
- The observation of cathode shell - this procedure is to check metal leakages, signs of hot spots, and shell deformation;
- Collect historical data of pot - Life, type and supplier of block, cathodic performance (CVD), metal quality, operating parameters;
- Visual inspection of cathode surface – identify cracks and spots of high erosion and metal leakage.
- Measuring of the height between cathode surface and deck plate – to quantify the level of erosion/wear rate;
- Dig out the cathode blocks;
- Photographic records of cathode section / measurement of cathode block position;
- Observation of lining materials aspects, points with metal or bath infiltration;
- Observation and measurement of deformation of cathode set;
- Autopsy report;

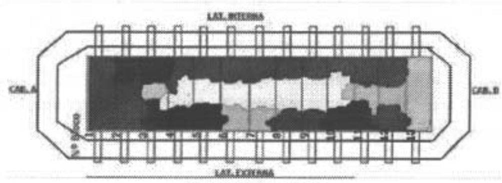
The figure 2 shows an overview of cathode blocks where is possible to verify a high level of wear mainly at the sides of cathode surface and the metal tapping area.



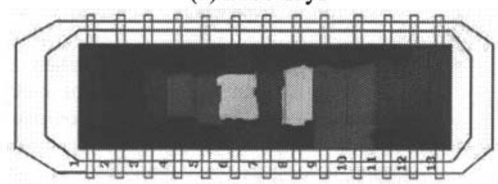
(c) 2600 days

Figure 2. Visual inspection of cathode block surface.

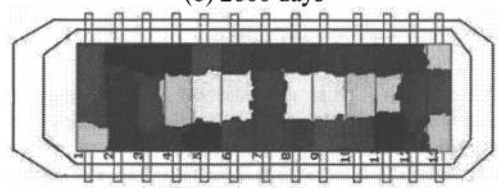
The depth of eroded area was measured in 180 – 210 mm deep. Figure 3 shows a schematic drawn of the measurements taken at cathode surface. As mentioned before the erosion in the metal tapping area is more severe than the center line of the cathode. It was also observed some cracks at metal tapping hole with some metal leakage.



(a) 2100 days



(b) 2600 days



(c) 2800 days

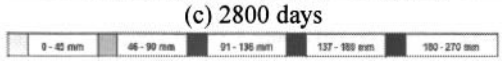


Figure 3 – Schematics drawn of the erosion level.

The high level of erosion was identified at blocks 4 and 5 at the metal tapping area, during the visual inspection of this area some cracks and aluminum leakage that reached the cathode bar was identified.

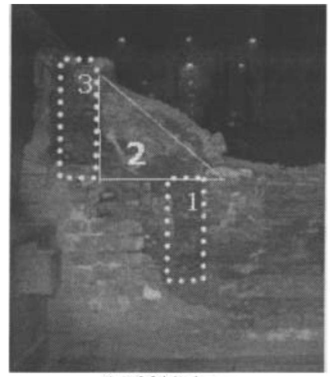
Due the high standard deviation of the measurements taken at the cathode surface it was not possible to establish a good conclusion between pot life and erosion paths. The results of erosion rate, average erosion and the critical point of the erosion are shown in table 2.

Table 2. Results from measurements taken at cathode

	Pot Life		
	2100	2600	2800
Distance from cathode surface to the cathode bar (mm)	37	5	46
Avarage Wear (mm)	89	176	121
Standard deviation of Wear (mm)	51	43	49
Wear rate (mm/year)	12	24	16
Bottom lining displacement	45	117	56

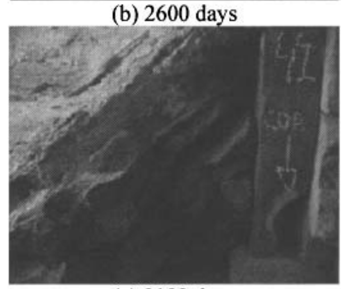
The side lining materials is an important element to cathode performance. These components should have good properties such as thermal conductivity, dilatometric and mechanical properties. The side ledge profile is strongly dependent on the thermal characteristic of pot design. The proper side ledge can avoid or minimize the erosion mechanism on the sides and on the monolithic materials.

The level of degradation of side lining materials was very different. The inspection showed that some particularities on the operation parameters might have an impact on the side lining materials performance, also, it was possible to identified some failure on the potlining procedures.



(a) 2800 days

(b) 2600 days



(c) 2100 days

Figure 4 – (a) 1 – monolithic big joint, 2 – side ramp, 3 – carbon side block, Lining materials in a such good condition; (b) high level of degradation of lining materials; (c) oxidation of side carbon block.

The figure 4a shows some bath leakage between insulation and refractory bricks. Some measurements taken at the cathode shell and cathode blocks indicate (see figure 4b) a linear expansion of cathode blocks implying in a compression of side lining materials. Monolithic materials is applied as an joint full fill material, and also have to be applied to prevent cracks of rigid materials such as cathode blocks during its expansion and to prevent metal/bath leakage. The autopsied pots showed a poor performance of this material due to the high level of "lamination" (ramming paste layer formation), caused by poor quality of tamping.

One of the most important items of the lining operation is the sealing of the voids on the cathode shell to avoid air attack that could cause thermal shocking and oxidation of the side lining materials. The figure 4d shows some consequences of the air attack.

An inspection on the bottom of cathode showed an intense transformation of silicon-alumina bricks. As known this is related to the "Sodium Swelling" that implies in an expansion of these bricks, this phenomena rises the cathode blocks up to 117 mm when compared with the standard project.

Harris and Oprea [2] have described the sodium swelling phenomena as a chemical reaction between sodium and constitutes of the fire bricks. A resume of these phenomena is shown below:

Equation 1: Chemical reaction between electrolytic bath and metallic Al.

$$Al_{(l)} + 3NaF_{(l)} = 3Na_{(C)} + AlF3_{(l)}$$

Equation 2: Chemical reaction between Sodium and Silica of refractory bricks

$$5SiO_{2(s)} + 4Na_{(g)} = Si_{(s)} + 2Na_2Si_2O_{5(s)}$$

Equation 3: Chemical reaction between Sodium and Alumina

$$2Al_2O_{3(s)} + 3Na_{(g)} = Al_{(l)} + 3NaAlO_{2(s)}$$

The phase formed in the equation 2 and 3 promotes a volumetric expansion up to 16% and 23% respectively, in instance part of the dislocation of cathode blocks could be explained by these phenomena. This volumetric expansion is showed in figure 5.

Figure 5. Dislocation of bottom lining up to 117mm.

Results and actions to maximize cathode life

For this study the pots were purposely shut down, the Fe and Si content in the metal pad was low, the CVD was considered normal for a pot age.

As a result of the autopsy the following points are considered as the most important:

- Identify the most eroded area;
- Measurement of the wear rate;
- Performance of monolithic materials;
- Performance of side lining materials such as fire brick and insulating materials.

Inspection of eroded areas

The visual inspection and measurements of eroded areas show the profile of erosion and its distribution on the cathode blocks. In figure 3 it is possible to identify the most eroded areas that occur at blocks 4 and 5. To minimize the effects of metal tapping some actions were deployed:

- Changing the metal tapping area each 6 months from blocks 4 and 5 to blocks 11 and 12;
- Keeping metal pad height as constant as possible to minimize the effects of metal movements to avoid an intense wear process;
- Training for operators responsible for metal tapping process to show the effects of non-compliance with operational standards.

Wear Rate

The calculated wear rate showed a wide range of variation, which implies in a poor correlation of cathode life. However, if the worst situation of average wear rate (176 mm/year) and assume the wear process as linear over the time the cathode life could reach up to 4,300 days. In 2010 only 3.5% of pots have reached more than 4,100 days.

Performance of the monolithic lining

The monolithic materials plays a key role in the performance of the pot, the main function of this component is to seal the spaces between the cathode blocks and the refractory lining to prevent infiltration of aluminum and electrolytic bath. Hiltman and Meulemann [3] showed that the dilatometric behavior of ramming paste may vary according to the heating rate and it could be strongly dependent on its formulation. Another aspect is an increase in compressive strength for different final temperatures of the baking process. Their study concludes for a good performance of monolithic lining must have the following characteristics:

- The applying process should be easy with minimal impact to health and the environment (ecofriendly);
- The behavior of expansion and shrinkage should be slight until the entire matrix undergoes carbonization;
- The compressive strength after carbonization must be less than in the cathode blocks.

Some aspects were observed in the autopsies:

- Layers of separation in the monolithic side ramp area, caused by excessive compression during application and inadequate heating rate;
- The level of wear in the small joint was very low than in the cathode blocks. It causes an irregular surface on the cathode blocks;

To maximize the performance of monolithic lining some actions were deployed:

- Increasing the pre-heating temperature for pot start-up from 680°C to 880°C in average and a better homogeneity temperature on the cathode blocks, side ramps and sub-cathode materials before the startup;
- Development of suppliers for ramming paste that could be applied at room temperature;
- Training of operators for correct installation of monolithic lining.

However, it was observed that the application of condensed collar at room temperature facilitates the work and minimize the impacts of thermal gradients between layers of ramming paste favoring a good adhesion of each paste layers.

Performance of insulation and fire bricks

To minimize the impacts of the "Sodium Swelling" on the refractory and insulating assembly some actions were developed as follow:

- Cup Test as a control parameter to evaluate the performance among different suppliers;
- Increasing the pre-heating temperature for pot start-up from 680°C to 880°C in average.

Harris and Oprea [2] have discussed the influence of Al_2O_3/SiO_2 relationship and the distribution of pores regarding to performance of lining materials. The study described the main mechanism of Sodium swelling and its effects on pot life. The Cup Test is measured by the total area of wear and Sodium attack, Figure 6 shows the main result of the test.
The Cup Test is a very reliable test, thus it can be applied to predict the lining materials performance and also as a tool to quality control of the lining materials.

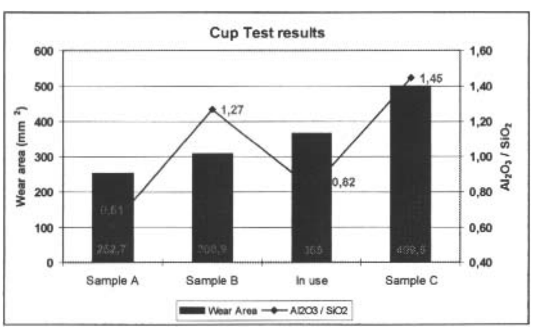


Figure 6. Results of Cup Test applied in a several sets of fire bricks and its behavior when it is exposed by Sodium attack.

Evaluation of side wall performance

The side wall is one of the largest thermal demand items in an electrolyte pot. The ledge profile is strongly dependent on the thermal performance of side wall. The freeze ledge is a kind of protective layer to prevent erosion and chemical attack of electrolytic bath and metal on the side wall materials.

Some aspects were observed during the autopsy. Erosion at the interface of bath / metal pad area was identified. Another weak point is the absence of freeze ledge formation at the top of the side wall. This is a consequence of alumina feeding process that is done by side crust breaker.

(a) (b)

Figure 6. (a) Crust breaker machine and its impact on side ledge formation; (b) Metal leakage on the pot side caused by absence o freeze ledge

The actions developed for the preservation of the side wall lining were:

- Training all operators on the standard feeding procedure and reinforce the impact of wrong operation on pot performance;
- Intensify the control of metal pad and bath level to minimize the effects of speed movement and its wear process on the side lining;

Conclusion

The overall pot autopsy showed an adverse situation indicating those particularities on operation procedures and the quality of lining materials that has an impact on pot life performance. The main remarks of this work are listed below:

- The high level of erosion is on the metal tapping area;
- The Sodium swelling process is one of the major concerns. The Cup Test is a effective tool that helps choosing the fire bricks with a lower Al_2O_3/SiO_2 proportion;
- It was not possible to have a good correlation factor between pot life and the level of erosion, to predict pot life more autopsies are necessary;
- The Cup Test showed to be a powerful tool with low cost and extremely reliable to choose lining bricks;
- The application and quality of monolithic materials should be inspect as in a regular basis,
- The pre-heating process is a key role for a good performance of lining materials and cathode life.

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