Essential Readings in Light Metals: Electrode Technology for Aluminum Production.
Edited by Alan Tomsett and John Johnson.

ALUMINIUM PECHINEY EXPERIENCE WITH GRAPHITIZED CATHODE BLOCKS

D. Lombard - T. Béhérégaray - B. Fève - J.M. Jolas

Aluminium Pechiney - LRF - BP 114 - 73303 St Jean de Maurienne Cedex - France

Abstract

For several years, Aluminum Pechiney has been testing graphitized cathode blocks on different types of pots in various smelters.

The theoretical advantages in using graphitized cathode blocks are presented, particularly the effect on potline amperage. Based on different industrial trials, a comparison is drawn with pots using conventional blocks, in terms of cathodic voltage drop, operational results and cathode life duration.

The performance of the different graphitized block qualities available on the market and the erosion phenomenon are also discussed. Finally, the economical interest of graphitized blocks is reviewed.

Introduction

Cathode blocks for the aluminium industry can be classified as follows: anthracitic and semi-graphitic blocks (containing anthracite, with or without graphite additions), graphitic blocks (100% graphite powder with pitch binder, baked at 1200°C max.) and finally graphitized blocks based on coke and heat treated at a temperature in excess of 2500°C. Due to the low graphitization temperature compared to that for electrodes, graphitized blocks are sometimes called semi-graphitized.

Among these different types of blocks, the graphitized ones are being increasingly used worldwide, especially for high intensity pots. Previous papers described industrial experience with graphitized cathode blocks [1, 2].

The first Aluminium Pechiney graphitized pots were started more than 40 years ago as a test but the economics of this technique were not obvious at that time. The real impulse came in the early 1990's. Nowadays, more than 200 pots operate with graphitized blocks in Pechiney smelters within the 100 kA to 300 kA range.

This presentation intends to explain the reasons for such a development, insisting on the specificities of the graphitized blocks and their advantages.

Introduction

Graphitized blocks exhibit interesting specificities compared with graphitic, semi-graphitic or anthracitic blocks (see table 1).

Table 1 : Typical physical properties of cathode blocks (along grain direction)

	Anthracitic/ Semi-graph.	Graphitic (<1200°C)	Graphitized (>2500°C)
Apparent Density	1.53 - 1.57	1.60 - 1.63	1.58 - 1.68
Open Porosity (%)	15 - 20	18 - 20	20 - 29
Bending Strength (MPa)	6 - 12	7 - 12	6 - 12
Electrical resistivity ($\mu\,\Omega$ m)	25 - 50	16 - 20	10 - 13
Thermal conduct. at 30°C (W/m.K)	7 - 18	25 - 35	110 - 130
CTE* 20-520°C (10^{-6}/°C)	2 - 3	2.8 - 3.3	2.5 - 4.5
Rapoport swelling (%)	0.3 - 1	0.1 - 0.3	< 0.05

* Coefficient of thermal expansion

- Sodium sensitivity: Numerous studies have confirmed the very low sensitivity of graphitized blocks to sodium impregnation [3, 4, 5]. Typical Rapoport swelling results are given in table 1. Block heat treatment has been shown to be a determinant parameter as far as Rapoport is concerned [3].
- Two other important graphitized block properties are the low electrical resistivity and the high thermal conductivity. Nevertheless, figures 1 and 2 reveal that these properties can change widely with temperature variations.
- Thermal shock resistance is also significantly higher for graphitized blocks.
- As far as mechanical properties are concerned, the major point to be noted is the relative softness of the graphitized cathodes. Abrasion resistance tests show that classically there are one to three orders of magnitude between the results of graphitized and anthracitic or semi-graphitic blocks, depending on the method [3, 6]. There are also differences between the various graphitized products available on the market, due to raw material and manufacturing process differences, some of these products being quite close to the graphitic materials (see figure 3).

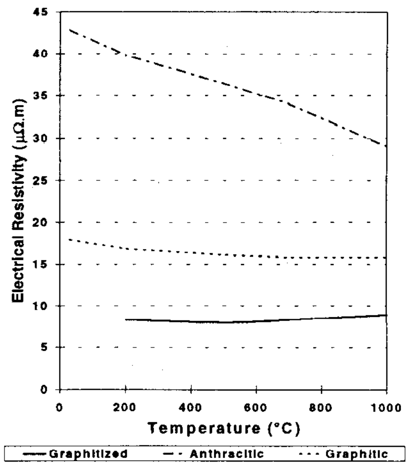

Figure 1 : Electrical resistivity of different cathode blocks (along grain direction) [7]

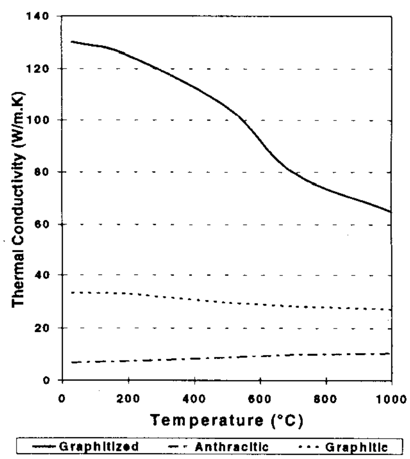

Figure 2 : Thermal conductivity of different cathode blocks (along grain direction) [7]

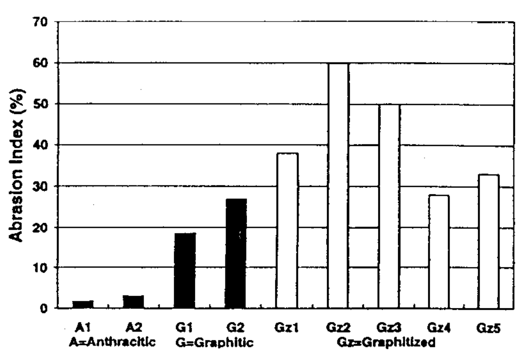

Figure 3 : Abrasion resistance for different cathode blocks - grinding method

- Finally, it must be pointed out that the available graphitized block grades can be either anisotropic or isotropic, depending on the raw materials (pet, pitch, regular or needle coke).

A few theoretical considerations

Mechanical aspects :

- Due to the low Rapoport swelling, one can expect to have no block lamination phenomenon, which occasionally occurs with other blocks, and slower block ageing.
- On the other hand, the lower abrasion resistance can induce accelerated cathode erosion due to metal movement.
- The higher deformation capacity of the graphitized products can induce lower sensitivity towards cathode cracking, in the event of heaving, for example.

Electrical aspects :

- The lower electrical resistivity implies a lower cathodic voltage drop.
- It also explains the current distribution modification in the metal pad, compared with the anthracitic or semi-graphitic cathodes. This leads to a new magneto-hydro-dynamic equilibrium of the pot.

Thermal aspects :

- The higher thermal conductivity implies a more isothermal cathode surface : the warmer block ends can be useful to avoid sludge deposits.
- Due to the low electrical resistivity of the graphite, which implies lower generation of energy in the cathode, an amperage increase can result in the same thermal equilibrium without the need for any additional bottom insulation. Figure 4 reveals the negligible difference in ledge profile for a 180 kA pot with semi-graphitic blocks and the same pot boosted by + 5.5 kA with graphitized blocks (validated calculations). The improved uniformity of the temperature within the graphitized blocks can be noted.

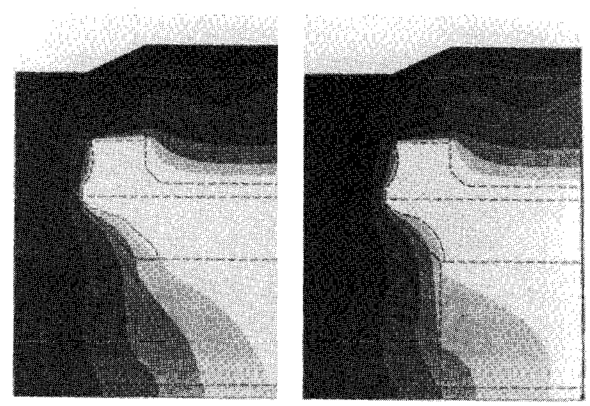

Figure 4 : Temperature distributions for a semi-graphitic (left) and a graphitized pot (boosted by 5.5 kA (right)

Graphite pot lining & start up

With graphitized blocks, specific attention must be paid to the cathode rodding, pot lining and pot start-up.

- Due to the lubricant properties of graphite, cathodic bars can slip out of rodded cathodic blocks during transport. Significant differences are also observed between the available grades, mainly due to thermal expansion coefficient differences. Such properties could be detrimental without adapted solutions.

- Another aspect to be considered is the high thermal conductivity of the graphitized block at room temperature, i.e. more than 100 W/m.K. At such a high value, the block preheating procedure before paste ramming must be adapted to reach the target temperature. This is more easily achieved with tepid paste (40°C) than hot paste.

- With electrical pot preheating, no changes have been noted for the preheating duration and the maximum surface temperatures of the cathode (850°C). Moreover, the cathode temperature ranges are cut in half at the end of the preheating period for graphitized pots compared to anthracitic or semi-graphitic pots. This is due to the higher thermal conductivity of the graphite, which also significantly decreases the risk of hot spots.

- The relatively low sensitivity of the graphitized blocks to sodium insertion allows a quicker rise in acidity during the first weeks after start-up. For semi-graphitic blocks, the maximum acidity increase is usually targeted at 2% per week [8] but with graphitized blocks, it is possible to go up to 4% per week for the first 2 weeks. With graphitized blocks, the start-up procedure duration can therefore be reduced by 2 weeks, starting from a neutral bath, or by 3 weeks starting from an acid bath (AlF_3 excess = 4%).

Technical results

a) Operating results

Table 2 deals with 3 different smelters using graphitized and anthracitic or semi-graphitized blocks.

For smelter B, the selected graphitized pots were not boosted, so the amperage increase is fictitious, calculated from the ACD increase. Thus, in this case, no total energy consumption result is given.

The amperage increase was very similar for both smelters, at around 2.6%.

At the same time, the current efficiency increased for the graphitized pots except for smelter C, which already exhibited a very high current efficiency (C.E.) with the anthracitic pots. This C.E. increase clearly indicates that the graphitized pots are more stable and relatively insensitive to pot operating disturbances. This fact is confirmed by the instability decrease in smelter A.

Table 2 : graphitized pot results with anthracitic or semi-graphitic pots as a reference.

	Plant A (300kA)	Plant B (280kA)	Plant C (180kA)
Amperage (%)	+ 2.7	+ 2.2	+ 2.8
CE (%)	+ 2.1	+ 1	- 0.5
Cathode drop (μΩ)	- 0.26	- 0.25	- 0.25
Energy from cath. drop. (kWh/t)	- 246	- 221	- 142
Energy from reducing ACD (kWh/t)	- 154	-	+ 48
Energy total (except due to CE)	- 400	-	- 94
Instability (nΩ)	- 11	+ 4	+ 1

As far as energy consumption is concerned, the results were as good as or better than those for the reference pots, despite the amperage increase.

b) Cathodic resistance

The interest of graphitized blocks with regard to cathodic resistance is quite obvious as illustrates by figures 5 and 6, showing boosted graphitized pots compared to semi-graphitic blocks.

Nevertheless, there are differences depending on the smelter.

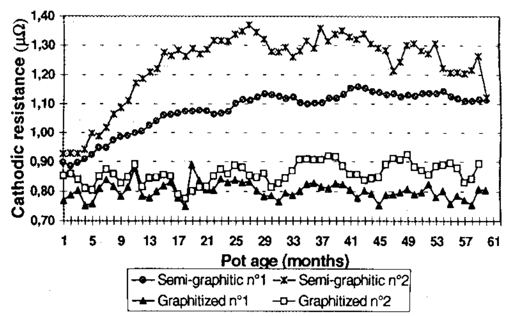

Figure 5 : pots with semi-graphite blocks and graphitized blocks (boosted)- smelter A

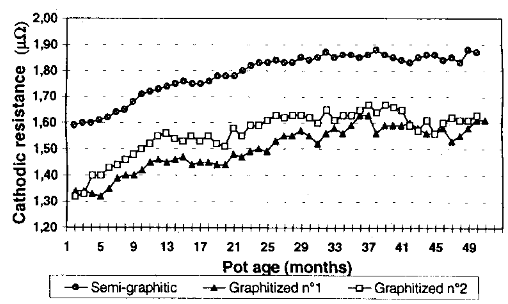

Figure 6 : pots with semi-graphitic block and graphitized blocks (boosted) - smelter C

Most of the time, the cathodic resistance remains very stable for the entire pot life when lined with graphitized blocks, but for smelter C, there was a continuous increase in resistance associated with sludge deposit (see figure 6). This is clearly demonstrated by the reverse effect of a metal height decrease after 40 months, which apparently also contributed to the reduction of the slight gap between the 2 grades.

Another illustration of the process parameter influence is given in figure 7 which deals with two graphitized pots operating in the same 280 kA technology smelter and started at the same time (unboosted pots).

The only difference in the lining materials was the cathodic block grade : one pot was lined with a pitch coke based block (n°1), the other with a pet coke based block (n°2). Their cathodic resistances evolved similarly.

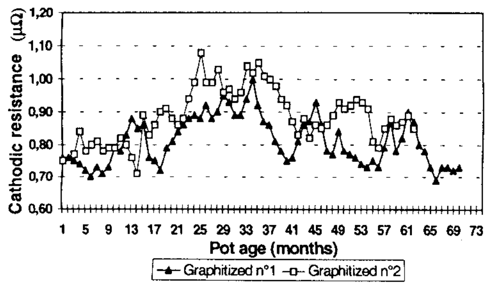

Figure 7 : pots with 2 different graphitized blocks (not boosted) - smelter B

c) Pot life

Figure 8 compares of two populations of pots : one with graphitized blocks and the other with anthracitic blocks. The very small standard deviation for the graphitized pots must be noted (less than 5 months). In this 180 kA smelter, the mean graphitized pot life (84 months) was better than that for the anthracitic pots.

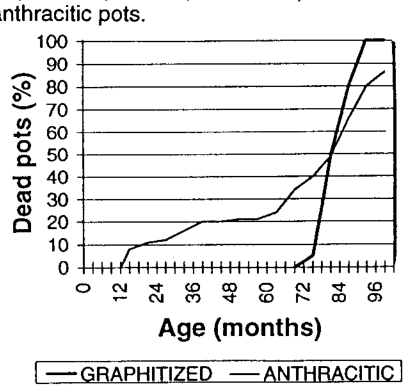

Figure 8 : pot life comparison between pots with anthracitic and graphitized blocks - smelter D

In another high amperage smelter using 2 different grades of graphitized blocks (60 first generation pots) and semi-graphitic blocks, the first graphitized pot death was obtained after more than 50 months, all the other pots being still in operation.

In a third smelter (300 kA), 2 different graphitized blocks were compared on 5 to 7 pots. After more than 65 months of operation, a majority of pots failed and the predicted average failure ages, about 65 months, are not statistically different.

From the graphitized pots tested in Pechiney smelters (more than 200), a very small number were stopped after less than one month. There were systematically either major vertical block cracks or aluminium infiltration in ramming paste joints. Defective blocks or non approved potlining procedures were found to be the relevant failure causes.

Apart from the above accidents, the main cause of pot failure was a locally accelerated cathode erosion in graphitized blocks, with collector bar attack and ironing.

As indicated hereabove, failures occurred at similar ages for graphitized and anthracitic blocks for a given smelter. It was also possible to reach excellent pot life, for example 114 months for a 130 kA side break test pot.

A typical block profile for an eroded graphitized block is given hereafter (see figure 9).

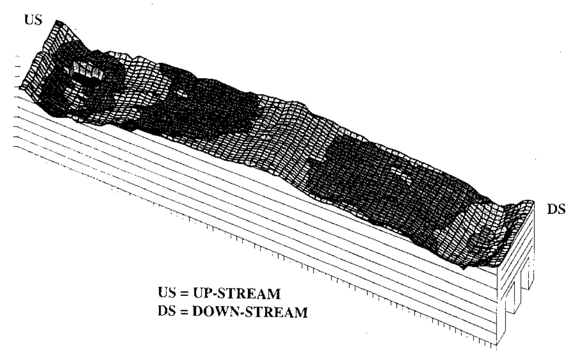

Figure 9 : Eroded graphitized block of a high intensity pot (61 months old) - smelter A.

Wear phenomenon

One minor consequence of the graphitized block wear is the increase in carbon content of the bath, with no notable effect on pot operation.

This wear must also be taken into account to maintain the thermal balance of the pot influenced by the metal height.

However, as previously noted, the most important consequence of cathode wear is the pot failure. This is the main cause of pot stoppage when lined with graphitized blocks.

Apparent wear rate (not corrected for cathode heave) can be easily measured on operating pots. Such measurements for one particular smelter are given in figures 10 and 11. Looking at these figures, one would expect pot life to reach 8 years. The same kind of extrapolations could be deduced from real mean cathode wear measured on stopped pots.

However, the limiting factor is the maximum wear rate. If we consider the population of all delined graphitized pots, the maximum wear rate values range from 2 to 6 cm/year.

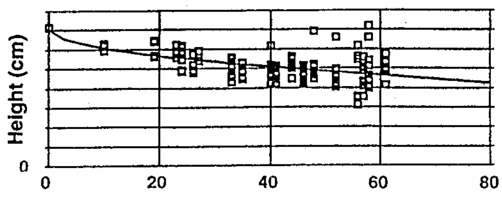

Figure 10 : Apparent wear rate for pots lined with graphitized block n°1(pots still operating) - smelter A

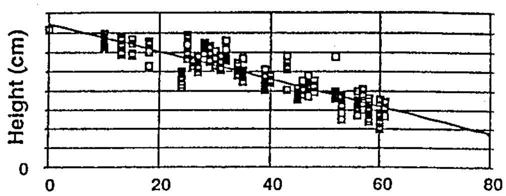

Figure 11 : Apparent wear rate for pots lined with graphitized block n°2 (pots still operating) - smelter A

Among the possible causes of block erosion, there are :

- mechanical wear,
- abrasion by alumina,
- metal movements,
- carbide formation/dissolution, or more generally, chemical attack.

Mechanical wear attributed to the crust grab can be put aside because the blocks are generally more eroded than the neighboring small joints. This is illustrated by figure 13.

Having said that, the key question is : which is the major erosion cause - abrasion or chemical attack ? Up to now, there were no conclusive answers.

Laboratory studies revealed that aluminum carbide formation kinetics were similar for graphite and anthracitic products [10, 11], whilst pore volume appears to be a major parameter [11]. Such results must be kept in mind when trying to understand measurements in pots.

Hereafter is a review and comment of the main observations that were made during graphitized pot delinings.

First, the maximal erosion area systematically occurs at the block ends, under the anodes, for side break as well as point feeding pots (see figure 12). The location of the maximum erosion area depends on the pot type. With point feeding high intensity pots, it is closer to the block ends than indicated in figure 12. This phenomenon is called the « W shape » erosion which should not be confused with potholes formed much faster and which have completely different shapes [9].

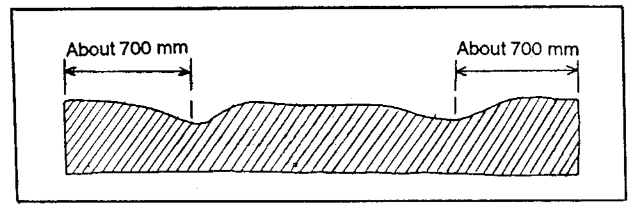

Figure 12 : Typical block profile for a 130 kA side break graphitized pot - smelter E

Secondly, the block is generally more eroded than the neighboring small joints (see figure 13). As previously mentioned, the ramming paste is systematically a tepid paste grade containing anthracite and pitch, thus more resistant to abrasion.

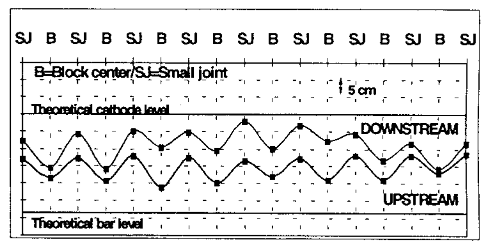

Figure 13: Longitudinal cathode profile by upstream and downstream block ends (measurements in the center part of each block and on each small joint)

Thirdly, there has been no case in our experience of excessive wear found at the tapping hole despite high metal movement. Curiously, it is not rare to find preferential wear in this area for anthracitic or semi-graphitic blocks.

Finally, no major differences were observed between the final cathode wear profiles compared for 2 different grades of graphitized blocks in two different smelters. Nevertheless, in both smelters, there were some differences in cathode wear uniformity. This observation has to be confirmed on more pots, but it must be noted that the two grades were completely different in terms of formulation (raw material, grain size distribution...). Figures 10 and 11 also reveal differences in the apparent wear kinetics for these two grades, but the measurements dealing with operating pots are not corrected for eventual cathode heave, which was also found with graphitized pots.

It must also be pointed out that despite significant block wear, it is not rare to encounter unusual difficulties for delining the pots, due to the fact that the blocks are not brittle enough. This can be linked to the observed lack of internal cracks inside old graphitized blocks.

Comparatively, such internal cracks are common for old anthracitic or semi-graphitic blocks, due to their relative sensitivity to sodium swelling.

Economical considerations

Obviously, the main economical interest of graphitized blocks is the additional production resulting from extra amperage, and in some cases from better current efficiency.

In all cases, despite the extra amperage effect, the specific energy consumption is equal or better than that for pots equipped with semi-graphitic blocks.

On the negative side, the accelerated cathode wear may result in a shorter pot life.

The cost of this marginal production can be estimated as indicated in table 3.

Table 3 : Economical calculations for 300 kA pots (hypotheses : amperage + 2.7 %, LME = 1500 US$/t)

Marginal cost	Unit cons.(/t)	Unit price ($/t)	Cost/t (marginal production) Same pot life	1 year pot life loss
Al2O3	1.92	200	384	384
Anodes	-	-	131	131
AlF3	0.018	800	14	14
Power (kWh)	11700	0.02	234	234
Potlining	-	-	82	300
Casthouse/melt loss	-	-	40	40
Total marginal cost ($/t)			886	1104
Yearly marginal production (t/pot)			22.3	22.3
Yearly net profit for 288 pots (MUS$)			4.0	2.5

The marginal cost of additional tonnage, as shown in the above table, is sensitive to pot life. However, at the indicated LME level, graphitized blocks are always profitable.

Conclusions

It can be concluded that graphitized cathode blocks are promising products for aluminium pots. Properly designed, constructed and operated graphitized pots can give significantly better technical performance, resulting in good payback, despite some more rapid wear compared with anthracitic or semi-graphitic pots.

Meanwhile, some differences in performance have been noted between graphitized block grades, in terms of technical results but these differences seem to be less marked than for anthracitic and semi-graphitic blocks [12].

Research efforts must now focus on the wear phenomenon. This implies close cooperation between cathode suppliers and smelters.

References

1. P. Aeschbach et al., Light Metals 1984, pp. 475-482
2. G. Newsted et al., Light Metals 1992, pp. 307-324
3. S. Wilkening et al., Light Metals 1981, pp. 653-674
4. Y. Mikhalev - A. Oye, Carbon vol. 34, n°1, 1996, pp. 37-4
5. C. Ozaki et al., Light Metals 1992, pp. 759-764
6. X. Liao - A. Oye, Carbon vol.34, n°5, 1996, pp. 649-661
7. D. Dumas - P. Lacroix, Light Metals 1994, pp. 751-760
8. M. Reverdy et al, Light Metals 1995, pp. 405-411
9. M. Sorlie et al, Light Metals 1992, pp. 299-308
10. E. Hollingshead et al., Light Metals 1982, pp. 625-634
11. K. Grjotheim et al., Light Metals, 1977, pp. 233- 242
12. JM. Jolas - J. Bos, Light metals 1994, pp. 403-411.