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

Graphite Cathode Wear Study at Alouette

Pierre Reny[1] and Siegfried Wilkening [2]
[1] Aluminerie Alouette Inc., 400 Chemin de la Pointe Noire, Sept-Îles, Québec, Canada
[2] VAW Aluminium-Technologie GmbH, P.O. Box 2468, 53014 Bonn, Germany

Abstract

Between 1996 and 1999, graphitized cathodes were installed in the 264 AP30 pots at Aluminerie Alouette Inc. aluminum smelter. During this period, an extensive cathode wear study was undertaken with the primary objective of predicting potlife.

A method to accurately measure cathode wear on an operating pot was developed. This method uses a surveyor's laser level equipment and is detailed in the paper along with measurements accuracy estimates.

The study is still ongoing but the analysis of the preliminary results show evidence that mechanical erosion, at the tapping hole or elsewhere in the pot, is not the leading wear mechanism. The large scale wear pattern suggests a current density-driven phenomenon, which is in agreement with electrical models. Fixed interval measurements of selected cathodes also show that the wear rate does not appear to vary with pot age, or potline amperage evolution as was the case at Alouette. The accuracy of this analysis method is such that it enables identification of areas where spalling of the cathode occurred at start-up.

Introduction

Aluminerie Alouette Inc. in Sept-Îles, Quebec, Canada is a greenfield aluminum smelter which started up in 1992 using 264 Aluminium Pechiney AP30 pots. After a very smooth start-up and first year of operation, problems showed up as some pots began to have red shells and to tap out through the sidewalls. Operation results analysis has shown a high correlation between cathode resistance increase and various operating problems including the red shell occurrence. Above a critical ohmic power input level, the pots showed areas where sidewall ledge was absent. This sidewall ledge loss not only caused the red shells, but also brought a host of operating difficulties, among them thermo-regulation instabilities, higher noise and further pot voltage increase compounding the problem. One known way to decrease pot heat generation, as described earlier (1,2,3), is to use the better conducting graphite as a cathode. Graphite disadvantages, mainly cost, mechanical strength and low-wear resistance were also well documented since the first trials of early 1960s.

The first graphitized cathodes were put in operation at Alouette early in 1996, as part of a cathode replacement program which lasted into mid-1999. Early graphite pot start-ups proved difficult since standard procedures for semi-graphitic pots led to cathode spalling. After improving start-up procedures and operation parameters, these problems were solved and it was found that graphite indeed held its promises and allowed sufficient ledge thickness while operating the pots at a satisfactory current efficiency. The main advantages found to be the result of using graphitized cathodes instead of semi-graphitic ones are:

- Cathode resistance decrease by 0,35 micro-ohm or more
- Pot stability (noise) improved by 20%
- Current efficiency increase of 1% (to 96.5%)
- Equivalent isopower amperage increase by 9% at same current efficiency
- Specific energy consumption reduction of 440 kWh/t at same amperage.

The shortened potlife possibly resulting from cathode wear then became the principal concern, therefore a wear monitoring program was started in 1997._

Measurement Method: Cathode Wear Measurement

F. Waldmann and C. Droste from VAW Aluminium- Technologie GmbH, developed a surveying method to measure cathode wear characteristics. The measurement apparatus and method are borrowed from standard surveying techniques, as described in figure 1. This measurement method was used to scan cathode surface exposed during normally scheduled anode change. For tapping hole measurement, the same method was used.

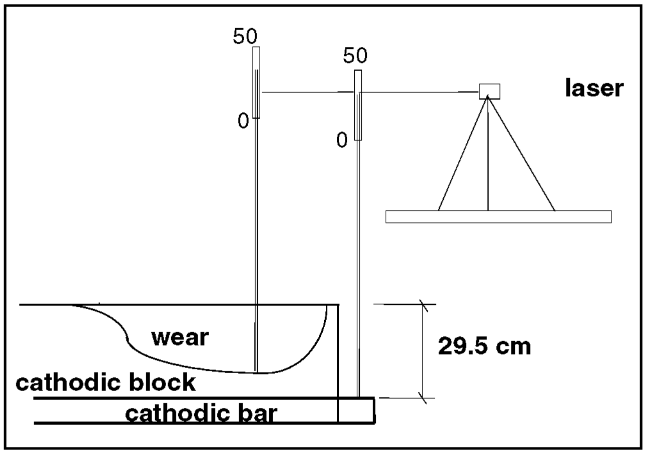


Figure 1: Cathode block erosion main measurement

One possible concern which could affect measurement accuracy is cathode heaving, which involves cathode bar displacement. In such cases for graphitized cathodes, heaving is associated with refractory bricks attack by bath material leading over time to a volume increase of the brickwork, which pushes the cathode blocks upward, causing the heave.

The measurement program was designed in two phases: first, establish the general wear pattern to locate the fastest eroding spots on the cathode. Second, make follow-up measurements on groups of pots to assess wear progression over time. Validation of measurement accuracy was done by measuring a stopped pot.

Figure 2: Cleaned surface of the graphite pot before delining.

Validation of measurement accuracy was done by comparing wear measurement taken with the live pot and comparing them with the real value taken during the delining of the same pot. So far, only one pot was stopped for validation. Results show that the wear measurement are within 1.5 cm of the real value.

Results

Wear Measurement Phase 1 - the Wear Pattern

For the first phase of the measurement program, the largest possible area of the cathode blocks were measured to obtain an idea of the general wear pattern. Anodes were removed and the cathode surface was measured at 20 to 30-cm intervals. The high temperatures and large exposed surfaces made these measurements quite a difficult task.

Even when measuring young (less than 500 days old) pots, the well-documented W wear pattern (6,7) showed up clearly as shown in figure 3a. Figure 3b represents the wear observed across the cathode blocks, showing the U pattern typical of cells where cathode blocks are joined by ramming paste. As already mentioned (6), the very presence of this shape indicates that mechanical abrasion possibly caused by the crust grab used at Alouette and other AP30 smelters is not the main wear cause otherwise, the ramming joints would have been shaved off.

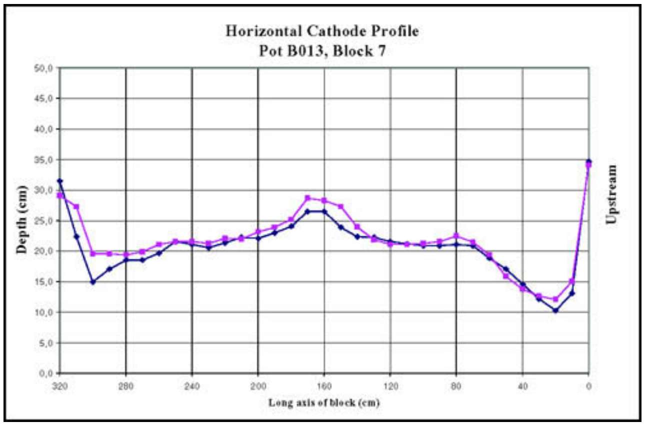


Figure 3a : Typical wear profile showing the wear pattern.

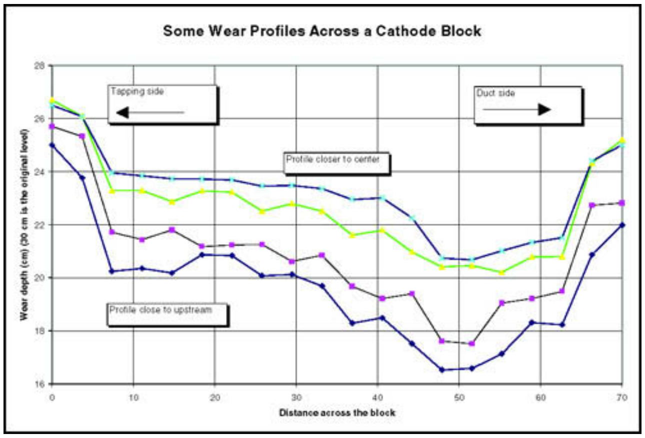


Figure 3b: Section across the short length of a cathode block.

Tapping hole measurements also showed that the mechanical erosion feared at this particular location does not happen at a critically high level. The wear rate there is minor compared to what was observed elsewhere in the pots. This corresponds with other observations (4) since the AP30 pot operates with low metal pad velocities and medium metal depth. See figure 4.

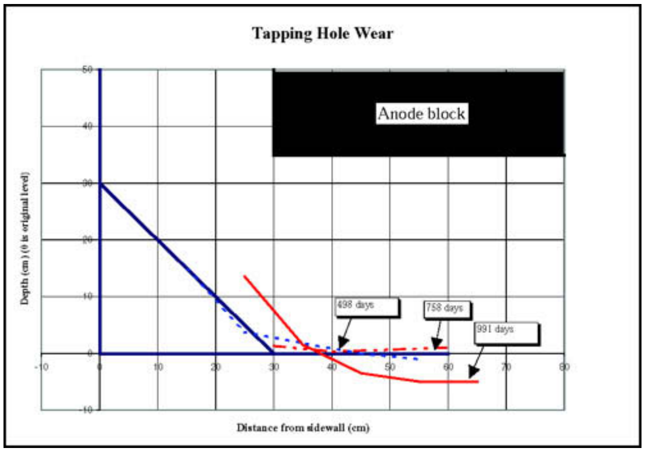


Figure 4: Tapping hole wear profile for pots of different ages.

Figure 5 shows a representative topography of one cathode block of the stopped pot. This general wear profile predicted by pure electric models based on the current density theory to explain wear rate (7) still does not apply evenly to all parts of the pot. Interesting local deviations from the general trend constitute more hints that wear rate is indeed strongly driven by current density.

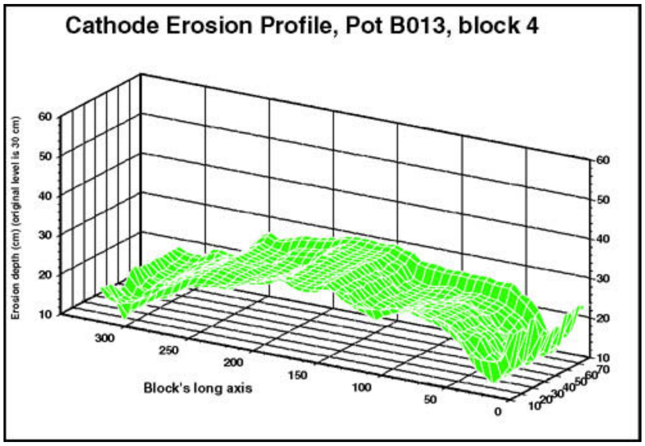
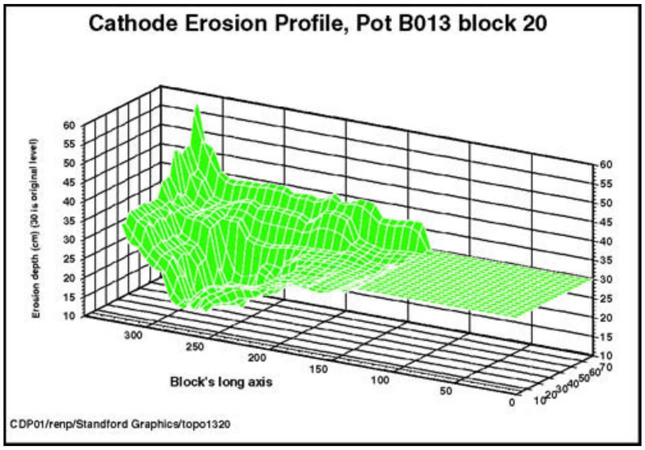


Figure 5: Typical wear topography of a cathode block.

1- The first deviation is caused by the presence of bottom ledge covering part of the cathode blocks at one end of the pot. Figure 6 shows the surface profile of such an end block. The remaining exposed graphite which had to bear the total block current experienced a higher than average wear rate despite the lower-than-average current load of this end block. The localized high current density can be in cause.

2- It is interesting to note that quite often the U-wear pattern is not symmetric: more carbon is removed above one of the two upstream cathodic bars in figure 3b, which correlates very well with cathodic current distributions taken before the pot was stopped. Again, a higher local current seems to accelerate cathode wear.



CDP01/renp/Standford Graphics/topo1320

Figure 6: Wear topography of an end block, showing the concentration of wear on the graphite surface not covered by ledge.

3- A fascinating observation of the eroded surface of a stopped graphite pot may give some clues about the involvement of mechanical erosion in the overall wear process. As shown in figure 7, the surface of the eroded graphite bears numerous small rounded holes 5 to 10 mm deep. These holes are not expected from a purely chemical-wear phenomenon, which tends to smooth out surfaces. Since the holes are not detached particles from the matrix (they are rounded through all matrix grains), some microscopic mechanical eddy-like erosion process may be at work. Despite the fact that sludge is not a problem with AP30 pots, it is quite possible that alumina particles spend some time in the deep cavities of the W trough and abrade the carbon while being transported by small eddies in the metal. As pointed out by Øye and Welch (5), both chemical and mechanical wear mechanisms seem to erode carbon.

Wear rate is thus dependent on location inside the pot.

Figure 7: Surface of the metal leftover peeled off the graphitized cathode of the stopped pot: the molding shows the holes on the cathode's surface.

Wear Measurement Phase 2 : Wear Progression over Time

The workload required by a measurement program intended to follow a large enough population of pots for every operating cathode type is far beyond reach for the small process control group at Alouette. We then opted for a ''potlife-oriented approach'' which would be designed to give the maximum wear rate for a pot, since the fastest eroding spot will likely be where the pot will eventually fail. Indeed, the ultimate goal of wear study is to predict cathode life as accurately as possible to ease budget planning and get efficient lining material inventory management.

Experience with phase 1 measurements and the stopped pot showed that fortunately the cathode is wearing faster at a convenient place for measurement, that is, close to the side of the pot. Figures 8 and 9 present typical results from these measurements for two cathode block types. Every wear measurement taken for the various high-speed wear blocks of the population pots are plotted against the age of the pots when measured. Despite a very high scattering of the data, evident differences of regressed wear evolution were observed between different cathode block types. Still, the high scatter made it very difficult to use these results for potlife prediction, since wear average and standard deviation at a given age would result in a standard deviation of the same order of magnitude as the potlife itself. This result is not satisfactory since operating experience of other smelters using graphitized cathodes with AP30 technology showed that potlife standard deviation is much smaller with graphitized blocks than with semi-graphitic blocks. Indeed, while semi-graphitic pots have potlife standard deviations around 400 days, graphite pots have around 100 days. This high scatter is at least partly caused by the location-dependent wear rate observed in the pots. Computed regression lines pass very close to the origin of the graph naturally, without ''help'' from parameter adjustment.

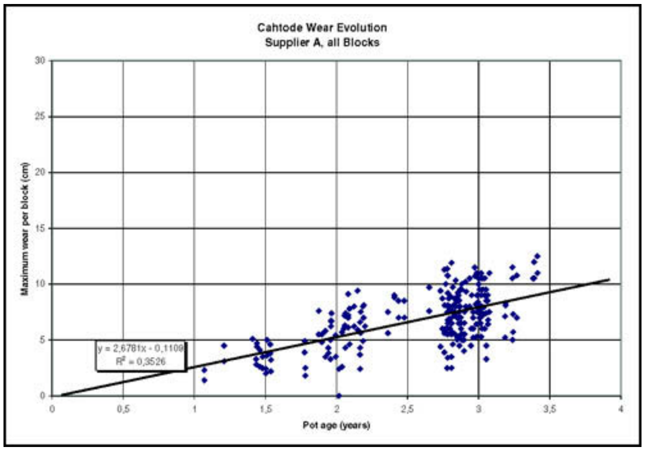


Figure 8: Wear measurements for a population of pots with supplier A cathode blocks.

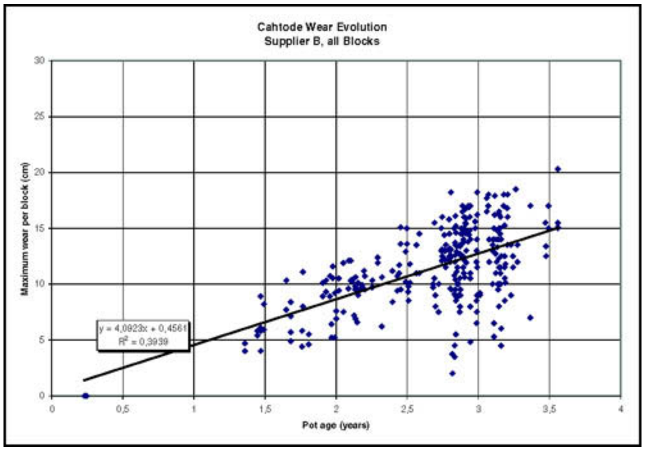


Figure 9: Wear measurements for a population of pots with supplier B cathode blocks.

Nevertheless, these first measurements led to create a wear map of the cathodes. All graphitized and graphitic blocks were seen to present a similar wear pattern. Only the average depth of wear varied for different cathode types of same age. This map can then be used to identify the fastest wearing spots of the pots, whatever the graphite type. Only those fast-wearing spots would have to be measured in order to assess maximum wear rate, and ultimately potlife. The measurement method is then very simple: the operator manually scans the open anode hole with the measurement rod during anode change. With the laser level in operation during the scan, he can rapidly find the lowest spot for each of the two cathode blocks made accessible by anode removal. He will only record the lowest level for each block and identify the block number; no other measurement for the exact location of this lowest spot is taken. This method is fast and does not cause stress to the operator nor the pot. In this manner, a single operator can easily take four measurements per hour if the pots to measure are close together. With only one operator, it is then possible to monitor meaningful populations per block type.

Analysis

A ''block-by-group'' study showed that within a given block type, plotting wear data for each block location of the pots produces graphs which have much higher determination coefficients, typically above 0.6. Figures 10 and 11 show examples of block-specific wear evolution for a given block type. The scatter is still too high to allow an analysis fine enough to tell between constant, decreasing or accelerating wear rate over time.

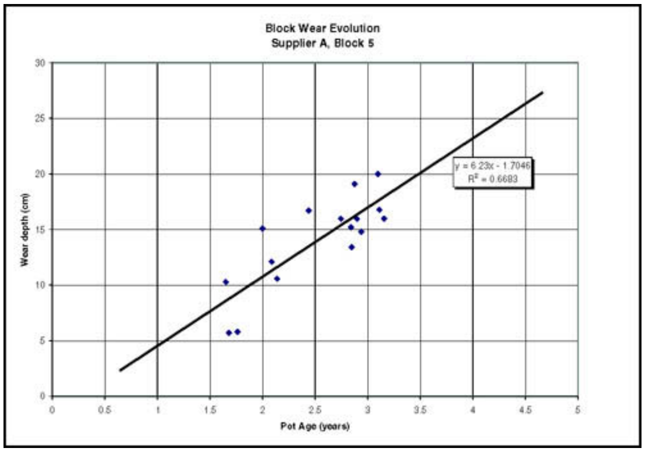


Figure 10: Wear rate evolution for block 5 upstream of the supplier A population.

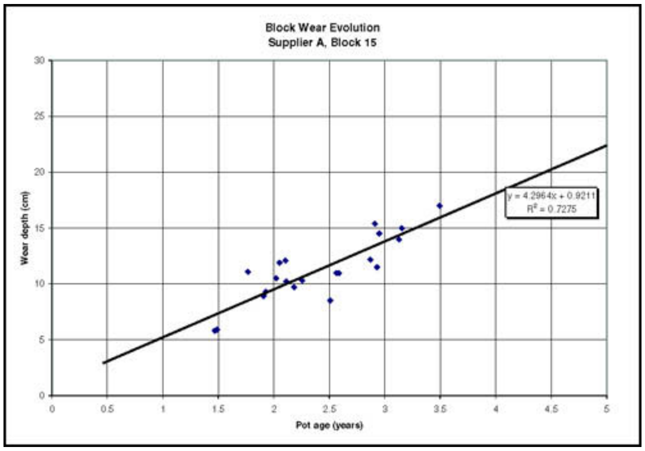


Figure 11: Wear rate evolution for block 15 upstream of the supplier A population.

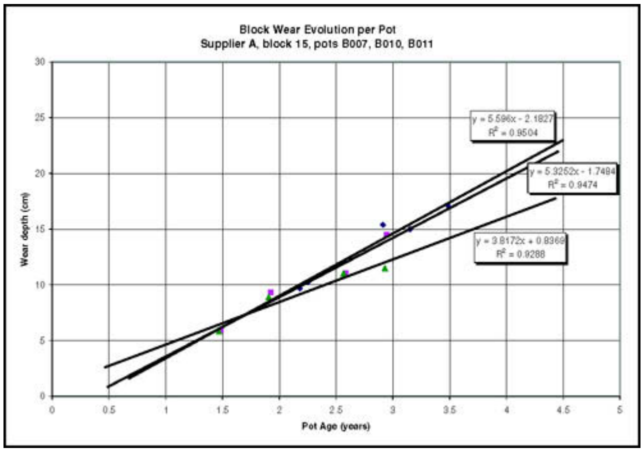


Figure 12: Individual wear rate evolution for block 15 upstream of three supplier A pots.

A "block-by-pot" study explains the scatter of the "block-by-group" graphs. As can be seen in figures 12, 13 and 14, taking maximum wear data for a single block from a single pot at various ages produce regression curves which are straight lines having very high determination coefficients, typically above 0.90. Figure 12 shows that the same block location in three different pots can wear at a rate varying by as much as 30%. Cathode bar current loads are well correlated with these wear-rate variations, but the initial cause remains unknown. Figure 13 represents an evident case of cathode heave, while in figure 14, spalling at start-up shows itself when regression line suggests that the cathode was already lacking almost 6 cm at zero age. Commonly, regression lines show a little heave with graphitized cathodes, and very linear wear evolution up to 1 200 days of age.

Figure 13: Early cathode heaving in a graphitic cathode.

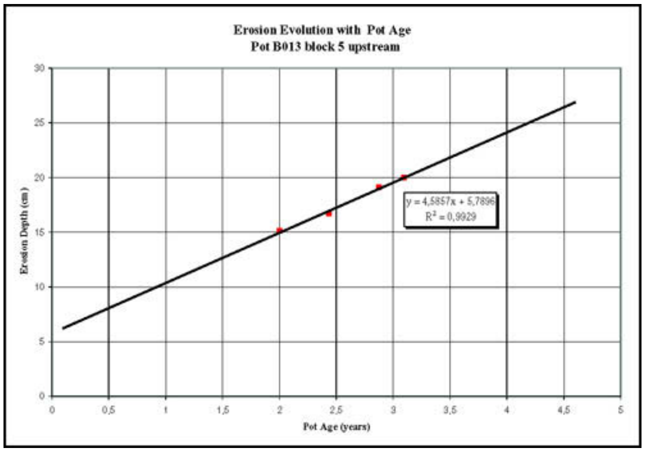


Figure 14: A case of known cathode spalling at start-up.

One possible cause of non-linear wear evolution is pot amperage variation, since wear is strongly dependent on current density. As it turns out, potline amperage, even if it varies by 10% or more, affects wear depth evolution very slightly: simulation (figure 15) showed that with wear rate directly proportional to amperage, this effect would be very hard to measure at Alouette, since the resulting curve is extremely close to a straight line.

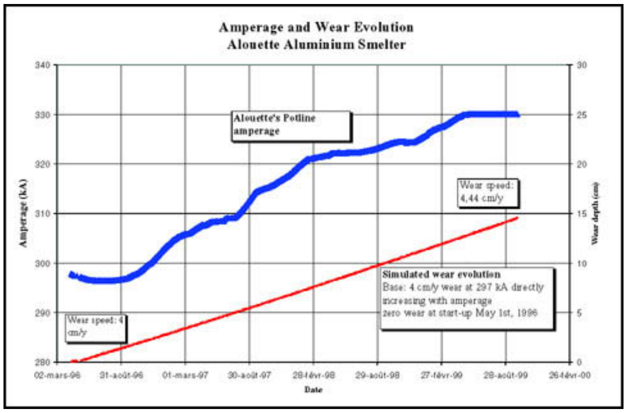
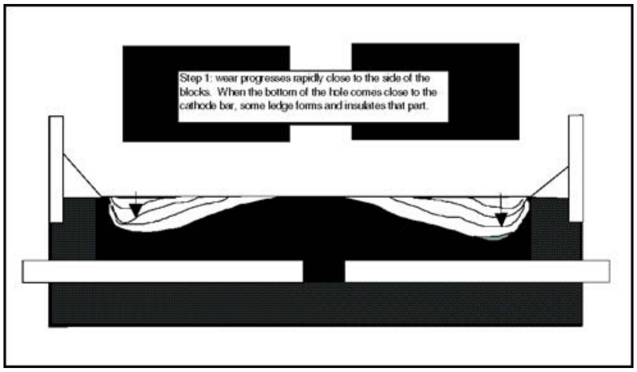
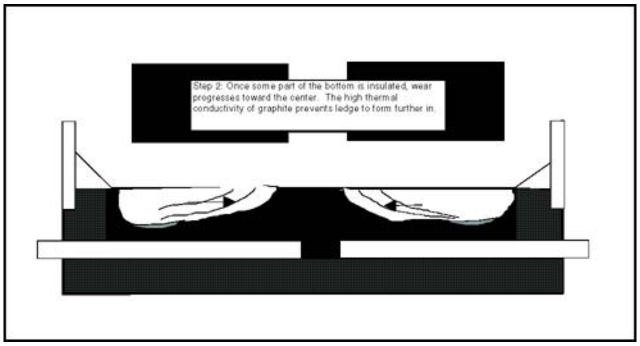


Figure 15: Wear-rate simulation showing that even a 10% amperage increase is not visible on a wear depth vs time graph.



Step 1: wear progresses rapidly close to the side of the blocks. When the bottom of the hole comes close to the cathode bar, some ledge forms and insulates that part.

Figure 16: Step 1 (linear part) of proposed wear mechanism.



Step 2: Once some part of the bottom is insulated, wear progresses toward the center. The high thermal conductivity of graphite prevents ledge to form further in.

Figure 17: Step 2 (flattened part) of proposed wear mechanism.

Recent measurements in the deepest worn blocks have shown that ledge or muck has formed in the bottom of the holes, which has never been observed in little worn blocks. Indeed, the manual scan is very sensitive: a rough surface is graphite and a smooth one is not. These measurements will result in a leveling of the wear progression graphs. Such results would explain the leveling out observed by Tabereaux et al. (9) at ages above 1 600 days. The high heat (or cold) flow in the collector bar (which is very close when wear has taken away more than 2/3 of the carbon above the bar) may cool the carbon enough to freeze some bath (or bath-alumina mix) present in the hole. The presence of bath between the cathode carbon and the metal pad is well documented. This insulating layer may force the current further in toward the center of the pot, thus spreading wear onto a larger cathode surface (figures 16 and 17 explain the proposed mechanism). Such a process could lead to increased potlife compared to what is expected from the early linear part of the wear evolution.

Conclusions:

These results provide a clear picture about cathode wear evolution and measurement:

1- Graphitized cathode blocks wear linearly in AP30 pots, at least during the first 1 200 days (3.5 years).
2- Cathode heave seem to vary between zero and 5 cm, a result obtained by bringing regression lines back to zero age: a negative value means that ‘‘excess’’ carbon is present early on in potlife. This result is confirmed by measurements of a pot which was stopped after one week: bath material had already converted a significant part of the refractory bricks laid under the cathode blocks.
3- Cathode spalling at start-up is easily put in evidence when the regression line hits a positive value at zero age: it means that some carbon was already missing from start ; this is, of course, a potlife decreasing factor since the slope of the wear curve is the same as for unspalled blocks at the same location in other pots.
4- Tap hole wear is not the main potlife threatening factor with high amperage graphite pots. High speed wear is concentrated on the side of the pots, and is fastest on some well-defined blocks, independently of the block type.
5- A mechanism is proposed to explain the leveling of wear when less than 10 cm of carbon is left above the collector bar.

References

1. Rapoport, M.B., ‘‘Uber die Vorgange in der Kathode der Aluminium Elektrolyse’’, Ubersetzung aus den Kohaazati Lopok, nr 7, 1958, 10 p.
2. Bacon, L.E., ‘‘Trend in Cathode Lining Materials’’, Extractive Metallurgy of Aluminum, vol. 2, 1962, pp. 461-483.
3. Bullough, V.L., Daly, L.O., McMinn, C.J., ‘‘Aluminum Cell Cathodes’’, Electrochemical Technology, vol 5, May-June 1967, pp. 182-185.
4. Liao, X., and ∅ye, H.A., ‘‘Physical and Chemical Wear of Carbon Cathode Materials’’, Light Metals, 1998, pp. 667-674.
5. ∅ye, H.A., and Welch, B.J., ‘‘Cathode Performance : The Influence of Design, Operation, and Operating Conditions’’, JOM, February 1998, pp. 18-22.
6. Lombard, D., Béhégégaray, T.,Fève, B., and Jolas, J.M., ‘‘Aluminium Pechiney Experience With Graphitized Cathode Blocks’’, Light Metals, 1998, pp. 653-657.
7. Dreyfus, J.M., and Joncourt, L., ‘‘Erosion Mechanisms in Smelters Equipped with Graphite Blocks- A Mathematical Modeling Approach’’, Light Metals, 1999, pp. 199-206.
8. Sorlie, M., and ∅ye, H.A., Cathodes in Aluminum Electrolysis, (Aluminum-Verlag GmbH, Dusseldorf), 1993
9. Tabereaux, A.T., Brown, J.H., Eldrige, I.J.,Alcorn, T.R., ‘‘Erosion of Cathode Blocks in 180 kA Prebake Cells’’,Light Metals, 1999, pp. 187-192.