# VARIABLE RESISTIVITY CATHODE AGAINST GRAPHITE EROSION

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## Abstract

Pre-baked electrolysis cells equipped with graphite cathodes exhibit a reduction in lifetime compared to cells built with graphitic grades. This limitation is clearly related today to a wear mechanism induced by an electrochemical reaction. The importance of the current density peak on the wear celerity has been highlighted and led to the development of new concepts aimed at a better balance of the current density in the cell. The variable resistivity graphite cathode is one of the most promising ways, which can be offered by the cathode supplier.
The actual technology development, resistivity pattern, current peak balance and erosion rate improvements are discussed through simulation models, products properties and in situ erosion measurements.

## Introduction

The widespread development of graphitized cathodes in high amperage pots in the 90's was a main step in the evolution of the aluminium electrolysis cell design.
On the positive side, it gave a boost to the cell amperage, an improvement in electrical stability and a lower and stable cathodic voltage drop (CVD). On the negative one, it revealed a new factor of cell lifetime limitation: a cathode wear process, also observed with other grades, but so rapid that it became the limiting factor of cell lifetime.
The wear mechanism leads to a specific erosion profile so called "W" shape whatever the amperage, the cell design and the block grade. As a result, cell lifetime is correlated to the maximum wear rate, recorded at the block extremity. Moreover, driven by this mechanism, lifetimes are so reproducible that it leads to a spectacular decrease of the standard deviation (1).
These observations were later confirmed in many other places, emphasised by the specific shape of the erosion profile and on the cathodic surface appearance and led to the conclusion that the erosion mechanism could not be a pure mechanical abrasion (2, 3, 4, 5).
In the 1999 TMS session, we first claimed the relation between the erosion profile and the distribution of the cathodic current density, showing with a numerical model the importance of both block electrical properties and rodding conditions on the current density peak (6).
This allegation has been, since, supported by many other observations and is now shared by most of the cathode producers (7, 8).
Efforts are now concentrated on the understanding of the wear mechanism and the improvement of product resistance to erosion.
As current density is driving the erosion process, solutions are sought to reduce the current density peak intensity. On one hand, smelters studied new techniques, mainly diffused by patent registration in the field of the collector bar design (9, 10). Even if basically attractive, none of these techniques has been claimed, up to now, to have reached an actual industrial extension.
On the other hand, and in line with the first trends presented in 1999, we went more deeply into the contribution to be brought by the cathodic block electrical properties. We soon raised the idea of a new graphitization technology aimed at creating resistivity heterogeneity along the cathode length. In order to modify current density distribution, the principle is to generate a resistivity pattern in the block that will thwart the current tendency to become concentrated at the block end. As resistivity is linked to the highest treatment temperature (HTT) achieved in the product during the graphitization process, we have modified the standard process to manufacture blocks where the resistivity depends on the location in the block.
The concept of the VRGC (Variable Resistivity Graphite Cathode) was born and further additional technical development led us to patent it in 1999 (11).
Even if still under optimisation, this new technique is now supported by sufficient behaviour performance in industrial cells to strongly believe that it could bring a significant reduction in the erosion rate and an economical increase in the cell lifetime.

## Modelling first approach

We used our electrical simulations model based on the commercial finite element Ansys® code presented before (6) to evaluate the effect of VRG cathodes on the cathodic current distribution and CVD.
Electrical models are run with block properties taken at 1000°C. Temperature patterns are not taken into consideration as graphite block resistivity variation with temperature at cell conditions is considered to be a second order factor. Moreover, we are looking at relative evolution of current density peak. Erosion pattern observations during cell autopsy revealed that eroded zones are localised between block extremity and 600mm from the block end (1).
For all the calculations the average current density (amperage divided by cathodic area) is equal. Current density distribution at the cathodic surface is calculated for the following configurations (vertical and horizontal refer to the block orientation in the cell).
The effect of the block resistivity property on the current density distribution along the cathode length is shown in figure 1.

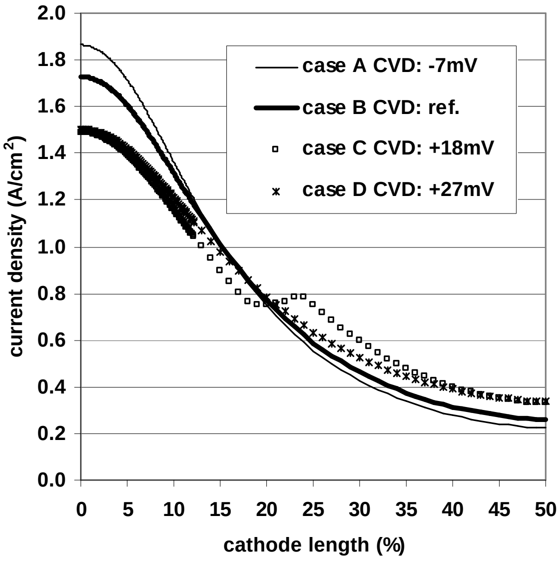

Figure 1.: Cathodic current density distribution along the length of the block according to the cathode grade

Case A: isotropic grade (equivalent vertical and horizontal resistivity) with a uniform resistivity value of 11µΩ.m at room temperature.

Case B: anisotropic grade (larger vertical resistivity than horizontal (ratio 1.2) with a uniform horizontal resistivity of 11µΩ.m at room temperature.

Case C: anisotropic grade as in case B with resistivity levels multiplied by 1.5 from block ends to 600mm inside the block.

Case D: graphitic grade

A promising current density peak reduction is observed. Maximum values can be reduced to those of the graphitic grade. Calculated CVD is located between the graphite reference case and the graphitic grade case. The door was open for further development of the concept and to industrial applications.

### Industrial process adjustment

The graphitization process is the main production step differentiating the graphite cathode from the carbon cathode. Graphitization is applied to a baked product, the HTT of which is about 800°C. Electrical power, typically 100kA and low voltage, generates heat in the furnace and allows it to reach high temperatures around 3000°C. This level is necessary to produce structural changes in the product: expulsion of hetero-atoms and of carbon crystal defects. One main consequence is the resistivity reduction. The objectives of the graphitization process are to reach a homogeneous temperature distribution inside the cathode itself, from one product to the next one in a furnace and from furnace to furnace.

During the last three decades the lengthwise graphitization process (LWG), where the cathodic blocks are assembled in a column and connected to a rectifier, has spread widely, compared to the bulk Acheson furnace.

Its advantages are lower energy consumption and improved working conditions. Figure 2 represents schematically the lengthwise graphitization process. The block columns are surrounded by an insulation pack in order to avoid electrical by pass and to limit thermal losses and product oxidation.

Due to better control of the current flow the lengthwise graphitization process achieves far better uniformity of resistivity within the block and also a better consistency in block population (6). This is highly dependent on the consistency of insulation pack properties and of the electrical contact between adjacent blocks. For this purpose, the columns are maintained under a regulated and adequate mechanical pressure during the successive shrinkage and expansion steps occurring during the graphitization process.

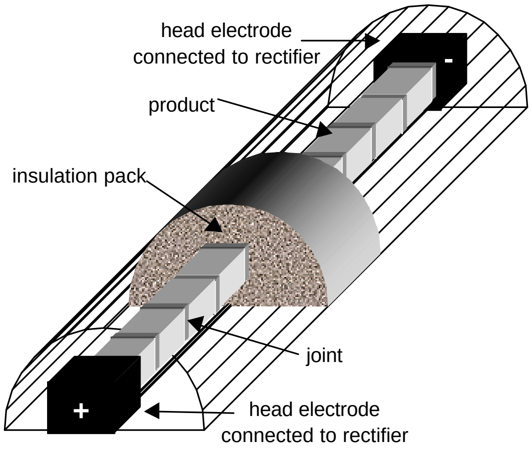

Figure 2.: Lengthwise graphitization process

Hence if the joint is too highly resistive, it will generate heat and consequently result in an increase of HTT at block ends. The resulting resistivity pattern will then favour a current density peak at the block ends, which is the opposite of the VRG cathode concept.

Additionally, this technique coupled with powerful rectifiers allows the operators to tune rather easily and precisely the level of resistivity over a large range even for large section blocks. Cathodes with resistivity levels from 8 to 15µΩ.m are easily produced.

The technological challenge of the VRG cathode was to master an intentional lengthwise heterogeneous resistivity while keeping all the advantages provided by the LWG process.

Experimental application successfully resulted in a regular production of cathodes for trial cells. As it might have been expected, this new technology still requires the adjustment of more accurate process parameters in order to ensure a good consistency in terms of production yield, and resistivity distribution.

Progressive experience has led us to believe that regular production of VRG cathodes is achievable.

### Actual block property results

Industrial VRG cathodes were prepared in order to adjust the process and then to provide cathodes for application in cells.

On some of these blocks, a destructive sampling was performed in order to analyse properties in different parts of the blocks and to establish a map of the resistivity level pattern.

Meanwhile, we developed a non-destructive control technique, based on eddy current measurement, offering the possibility of controlling, on a regular basis, the resistivity gradient on all blocks. A good correlation was proven between the non-destructive and destructive methods (fig. 3). This technique provides an effective and rapid tool to characterise production and to evaluate the effect of process parameters on resistivity pattern and production consistency.

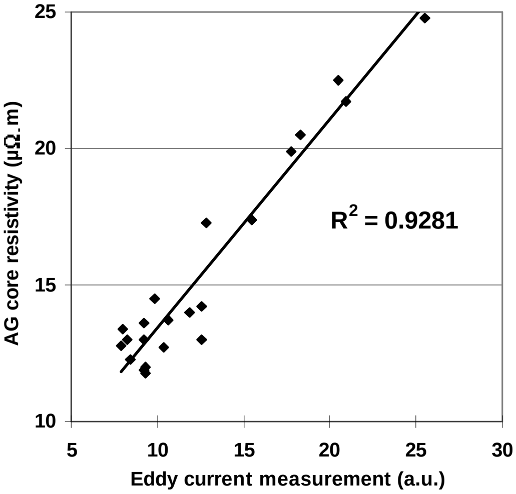

Figure 3.: Correlation between eddy signal and resistivity measurement after coring at the eddy probe location

As the ultimate objective is to create a resistivity gradient in the product through a temperature (HTT) heterogeneous pattern, it is necessary to quantify the dependence between these two parameters. Cores were treated at different temperatures and then measured for resistivity at room temperature (fig. 4).

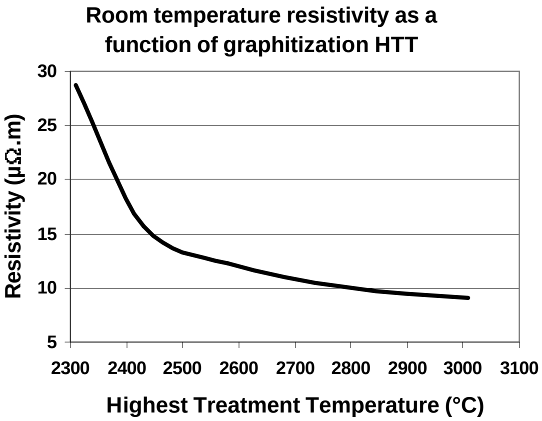

Figure 4.: Effect of HTT on room temperature resistivity

The variation of resistivity with HTT is non-linear showing a smaller dependence on temperature at high temperatures. It provides temperature gradients required during the graphitization process in order to obtain a reasonable resistivity gradient in the cathode. It shows also, that resistivity dispersion may increase when HTT decreases, as the absolute value of the slope of the curve increases in the lower temperature range. Another consequence can be deduced: the resistivity gradient is more difficult to achieve when lower block average resistivity is requested. In other words, for the same temperature gradient, the resistivity gradient is reduced when average HTT is higher. Different graphitization parameters will then have to be applied to such various production targets.

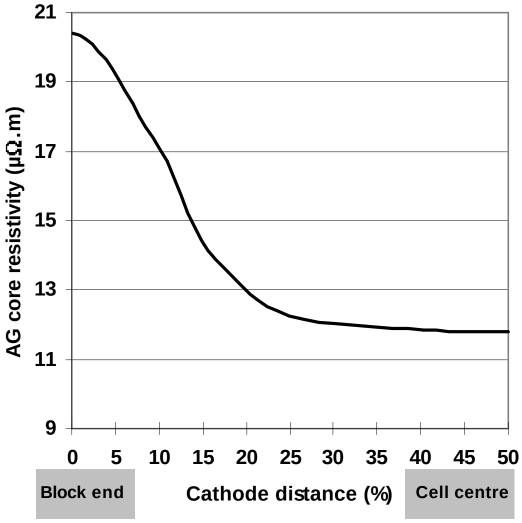

Figure 5.: Resistivity pattern of typical VRG cathode

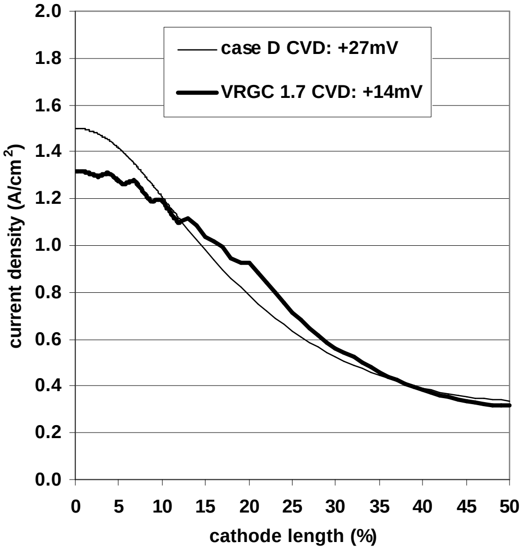

Figure 6.: Calculated current distribution obtained with actual resistivity pattern of VRG cathode, compared to graphitic cathode

The resistivity pattern, obtained by core sampling and represented in figure 5, was tested in our current distribution model and it demonstrated that such blocks are able to improve current distribution in the electrolysis cell (fig. 6).

As a general conclusion, both experimental results and numerical simulation led to the conclusion that a VRG cathode production was feasible and effective in reducing the current density gradient in the cell. A resistivity ratio between block extremity and block centre of 1.5 to 1.8 is achievable on a regular basis, with a basic average resistivity ranging from 8 to 11.

## Process optimisation

The impact of the heterogeneous resistivity pattern was analysed in our current distribution numerical model. Parameters like the length of the high resistivity zone, the level of resistivity in the block extremity, the ratio between the extremity resistivity and the centre resistivity were studied in order to arrive at the optimum resistivity pattern

The following figure refers to two values of the resistivity gradient. As shown, the larger the resistivity gradient the lower the current density peak but the larger the CVD. A compromise will have to be found according to economical objectives (fig. 7).

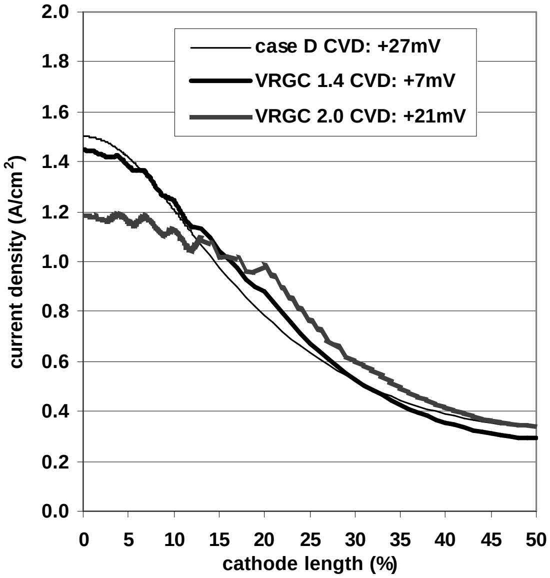

Figure 7.: Current distribution as a function of resistivity gradient amplitude

The numerical simulation is very useful to forecast process parameter effects and design the new graphitization technique. It is possible with our process to tune the resistivity pattern. For example, we can lower the resistivity in the centre of the block in order to reduce the CVD and keep the advantage of a more even current distribution.

## Properties of the high resistivity zone of the block

Before testing VRG cathodes in cells, it was necessary to verify the impact of the thermal gradient on properties other than resistivity. HTT also influences the thermal conductivity, flexural strength, CTE and sodium swelling characteristics. Sampling and characterisation were performed at block ends and at the block centre in order to quantify property gradients. Results are reported in table 1:

| | | | VRG cathode property | |
|---|---|---|---|---|
| | | | high resistivity ends | low resistivity centre |
| apparent density | | g/cm$^3$ | **1.63** | **1.62** |
| H2O porosity | | % | **20** | **21** |
| real density | | g/cm$^3$ | **2.18** | **2.20** |
| ash content | | % | **1.0** | **0.8** |
| electrical resistivity | WG | $\mu\Omega$.m | **18** | **10** |
| | AG | | **21** | **12** |
| thermal conductivity | WG | W/m/K | **104** | **152** |
| | AG | | **78** | **104** |
| flexural strength | WG | MPa | **14** | **14** |
| | AG | | **11** | **9** |
| CTE | WG | $10^{-6}$/K | **3.1** | **2.8** |
| | AG | | **3.3** | **2.7** |
| Na swelling | AG | % | **0.10** | **0.05** |

Table 1: Variable Resistivity Graphite Cathode properties

The table shows no major property change, except for resistivity and thermal conductivity, which are related, between the two locations in the block. Block ends are therefore slightly higher in CTE, sodium swelling and mechanical properties.
These results inspired confidence in the extension of the concept to industrial electrolysis cells. Trial cells were started to determine if such blocks with heterogeneous properties could withstand cell-operating conditions.

## Performances in cells

The purpose of the VRG cathode is exclusively to reduce, at the block extremity, the maximum erosion rate and to increase correlatively the life of the cell. As longer lives are expected, feedback from smelters may take several years.

Initial trials of the VRG cathode in cells were performed in order to ascertain the feasibility of such a concept. Firstly it is mandatory to confirm that no detrimental side effect could be induced by property gradients. Secondly it was necessary to confirm the stability of the cathodic drop and the operating parameters at levels comparable to other graphite grades. Figures 8 and 9 present examples of actual results, giving full confidence in the performance of these pots.

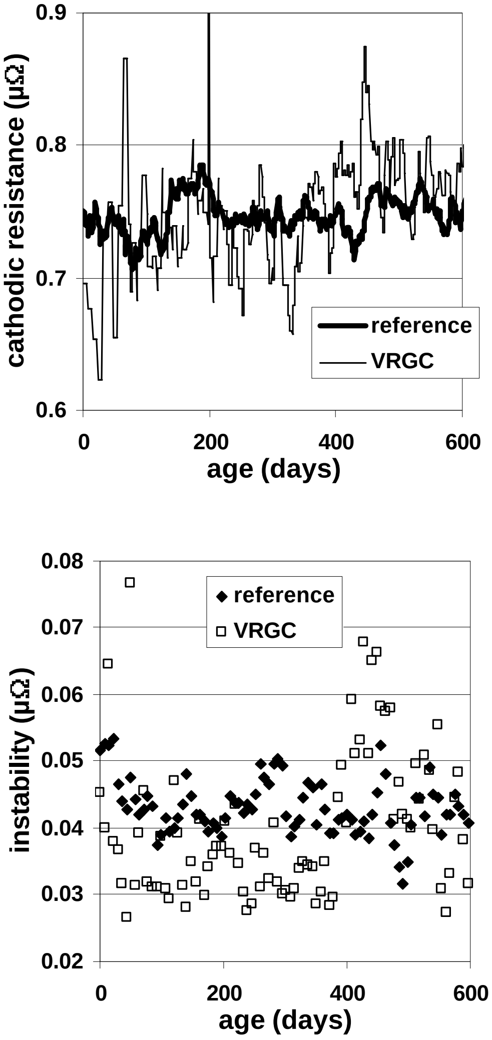

Figure 8.: CVD and instability evolution of VRC cathode compared to standard grade (by courtesy of ALUMINERIE ALOUETTE INC.)

We are now secured with more than twelve cells in operation, in differing technologies, equipped with the VRG cathode, the oldest being over 3 years. Even if some of these cells have not reached a sufficient age to draw definitive conclusions, some trends and partial answers to our concerns can already be highlighted:

- Perfect behaviour of the VRG cathodes to all stresses induced during the preparation and early life of the cell (casting, preheating, and start-up).
- Normal cell thermal balance with no significant change in cell parameters. The CVD increase predicted by the numerical model is not confirmed.
- Observation of a tendency toward decreased erosion rate through in situ measurement. A reduction of 25%, compared to standard graphite grades, was mentioned in one smelter, after one year of lifetime. These results have to be confirmed, as the age of the cells increases.

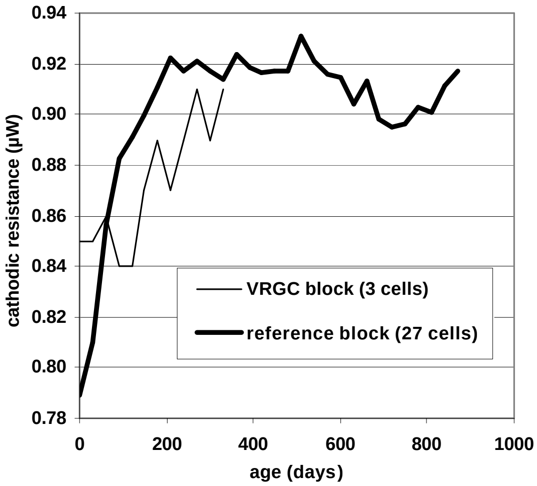

Figure 9.: CVD evolution of VRGC block compared to standard grade (by courtesy of ALUMINIUM BAHREIN B.S.C. company)

Confirmation of these results will provide strong support to this basic concept developed from the numerical simulation approach.

## Conclusion

Following the hypothesis that erosion of graphite cathode grades is linked to current density, we have developed a new concept of graphite cathode: Variable Resistivity Graphite Cathode. In this cathode, the resistivity is higher at the ends of the block than in the centre. Numerical simulations of the effect of such a resistivity distribution on current distribution, based on actual resistivity values, show that we might expect a significant reduction in the maximum current density with a negligible change in cathodic drop. The current density peak can be reduced down to a level comparable to a graphitic grade, leading to an expectation of a lifetime equivalent to that of a graphitic grade.

VRG cathodes are being tested in several smelters since a few years ago. No detrimental effect of property gradients in the blocks has been recorded. Hence, while still young, some cells are showing promising results in terms of the erosion rate.

The treatment leading to the Variable Resistivity Graphite Cathode, performed during graphitization, presents the advantage of being applicable to all graphite grades. Therefore it is possible to accumulate its positive effect with other improvements, which have been and will be brought to cathode blocks. This new graphitization technique, which can be fine tuned to cell characteristics, is a very promising additional contribution to the reduction of the erosion rate of graphite blocks and to the increase of the lifetime of high amperage cells.

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