

Development of a New Type of Cathode for Aluminium Electrolysis

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Abstract

Over the past decades, aluminium smelting industry has been increasing significantly its productivity, producing more aluminium per day with lower energy consumption. In this race toward higher the productivity, cathode producers have played a major role with the development of highly conductive cathodes. Indeed, from the older anthracitic cathodes to the newest graphitized cathodes, the electrical resistivity has been divided by 5, leading to lower electrical losses. In recent years, the use of copper in the collector bars has changed the game. With this technology, the heat loss from the cell can be excessive. Consequently, there is a renewed interest for cathodes with intermediate properties, from the older smelters for increasing their productivity and from newer smelters for optimizing their thermal balance. In 2012, it became evident that a new way to produce intermediate properties cathode blocks was needed in order to supply the market. Carbone Savoie has launched an R&D project to adapt to this demand. After a few industrial trials, the targeted electrical resistivity was reached. A complete characterization of the product, including tests at high temperatures, made us confident that a new way was found to produce intermediate properties cathodes. And the cathodes were tested in electrolysis cells.

Keywords: Aluminium electrolysis cells; Cathode; electrical resistivity of cathode blocks; graphitized cathode blocks; high temperature properties of cathode blocks.

1. Introduction

In the aluminium electrolysis cells, the cathode blocks play a major role in the performances of the cell. Indeed, the electrolysis is performed in a molten salts bath at 960 °C and the cathode has to withstand this environment, preventing the leakage of the bath or the molten aluminium. It also has to carry the current. Carbon is an inert material, refractory and conducts current. Thus, it is a good candidate to face these constraints. Until now, only cathodes based on carbon are used industrially at an acceptable cost.

As soon as the cathode fails, the electrolysis cell has to be stopped and relined with new materials. So the resistance of the cathode to the internal environment of the cell is of importance as the cathode wear triggers the end of pot life. Also the thermal and electrical properties of the cathode directly influence the thermal and electrical losses of the electrolysis cell. The design of the electrolysis cell takes into account these properties.

2. Different Cathodes Based on Carbon for the Aluminium Industry

The cathodes based on carbon are made of dry aggregates, usually anthracite, graphite or petroleum coke. These components are sieved, grinded and mixed, following a precise recipe, and bound together with a binder having a high coking value, usually coal tar pitch. High temperature treatment cokefies the binder, making the mix solid and electrically conductive. Final machining is then performed. The process is summarized in the Figure 1.

Depending on the origin of the aggregates and their highest treatment temperature (HTT), very different properties can be achieved. The cathodes are usually sorted into two families:

- The carbon family where the dry aggregates and the binder are heat treated at about 1 000 °C;
- The graphitized family, where after a first baking, the aggregates and the binder are heat treated at about 3 000 °C in graphitization furnaces.

2.1. Carbon cathodes

In the carbon cathodes family, the electrical resistance varies with the graphite / anthracite ratio. The higher the graphite content, the higher the conductivity and also the higher the cost. Anthracitic cathodes have a resistivity of about 45 $\mu\Omega\text{m}$; with 100 % graphite, graphitic cathodes resistivity decreases to about 20 $\mu\Omega\text{m}$.

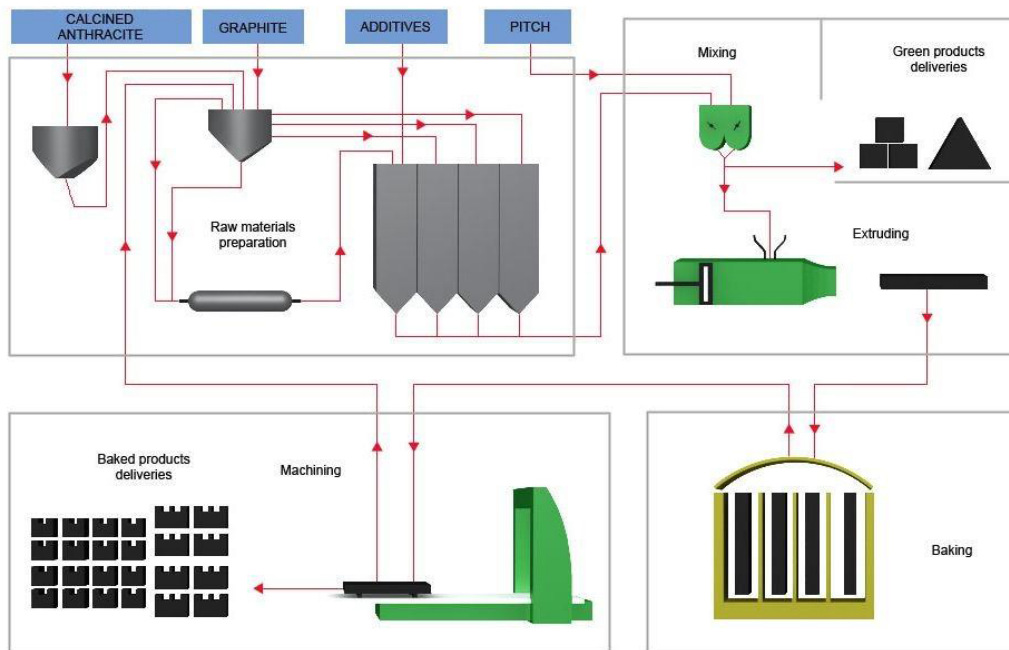


Figure 1. Sketch of the carbon cathode manufacturing.

2.2. Graphitized cathodes

To decrease further the electrical resistivity of the cathodes, another step in the process is needed (see Figure 2). Thanks to Joule effect, the cathodes are heat treated to 3 000 °C. This increases the order in the carbon planes and removes the hetero-atom, leading to a better electrical conductivity. However, this extra-step is energy consuming: between 2 and 8 kWh/kg are needed, depending on the process and the targeted HTT. For cathodes, the graphitization process decreases the resistivity of the product from 35 - 40 $\mu\Omega\text{m}$ down to 10 $\mu\Omega\text{m}$. Lower resistivity of 8 $\mu\Omega\text{m}$ can be achieved by increasing the HTT. On both cases, the lower cost of the raw materials used, typically petroleum coke, doesn't offset this extra-cost.

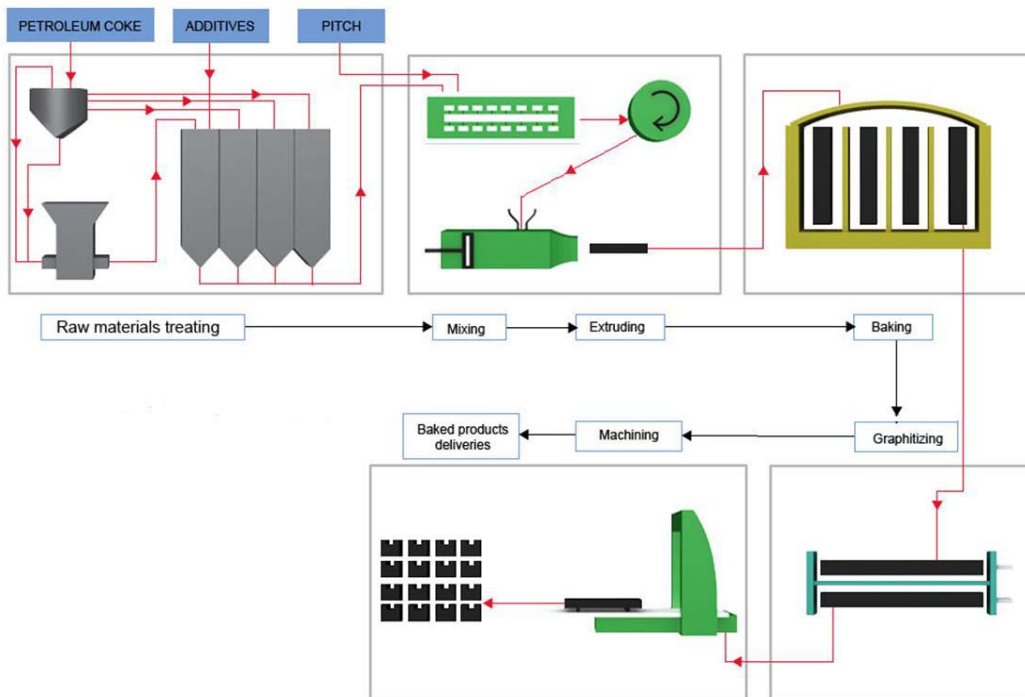


Figure 2. Sketch of the graphitized cathode manufacturing, showing the extra step of graphitization.

2.3. Cathode properties

The comparison of the properties of different kind of cathodes actually used is presented in Table 1. In the end, the more conductive the cathode is, the more expensive it is. Anyhow, the cathode price accounting for less than 1 % of the costs of aluminium produced in the cell, the electrical gains achieved with the use of the conductive cathodes is significantly profitable.

Table 1. Typical properties of different kind of cathodes. Semi-graphitic and graphitic are carbon cathodes (baked at 1 000 °C). Graphitized cathodes are heat treated at 3 000 °C.

| CHARACTERISTICS | | Semi-graphitic | Graphitic | Graphitized |
|-------------------------|---------------------|----------------|-----------|-------------|
| Apparent Density | | 1.55 | 1.60 | 1.73 |
| Ash Content | % | 2.0 | 1.0 | 0.2 |
| Flexural Strength | MPa | 10 | 9 | 13 |
| Electrical Resistivity | $\mu\Omega \cdot m$ | 30 | 20 | 10 |
| Thermal Conductivity | W/m/K | 14 | 30 | 125 |
| Sodium Expanding Effect | % | 0.5 | 0.3 | 0.1 |

3. Evolution of the Cathodes Market along the Years

3.1. Move towards more and more conductive cathodes

Thanks to their profitability, all the new smelters built in the western world have been installed with graphitized cathodes since many years. For the aluminium smelters already started years ago, the swap from carbon cathodes to graphitized cathodes cannot be done without significant change. Indeed, graphitized cathodes have high thermal conductivity and low voltage drop, which may lead to bottom freezing. The bottom freezing can eventually increase the voltage drop to a higher value than carbon cathodes. However, usually, with the progressive amperage increase and some small design changes, the more conductive cathodes progressively replace the less conductive ones without causing any backlash [1].

In general, there is a trend to move from semi-graphitic to graphitic and finally to graphitized cathode blocks. This trend has been observed in many smelters, and can be visualized with the cathode sales performed by Carbone Savoie, presented in the Figure 3. In this moving environment, the graphitic cathodes demand is staying around 20 ktpy, whereas the semi-graphitic demand decreases and the graphitized demand increases.

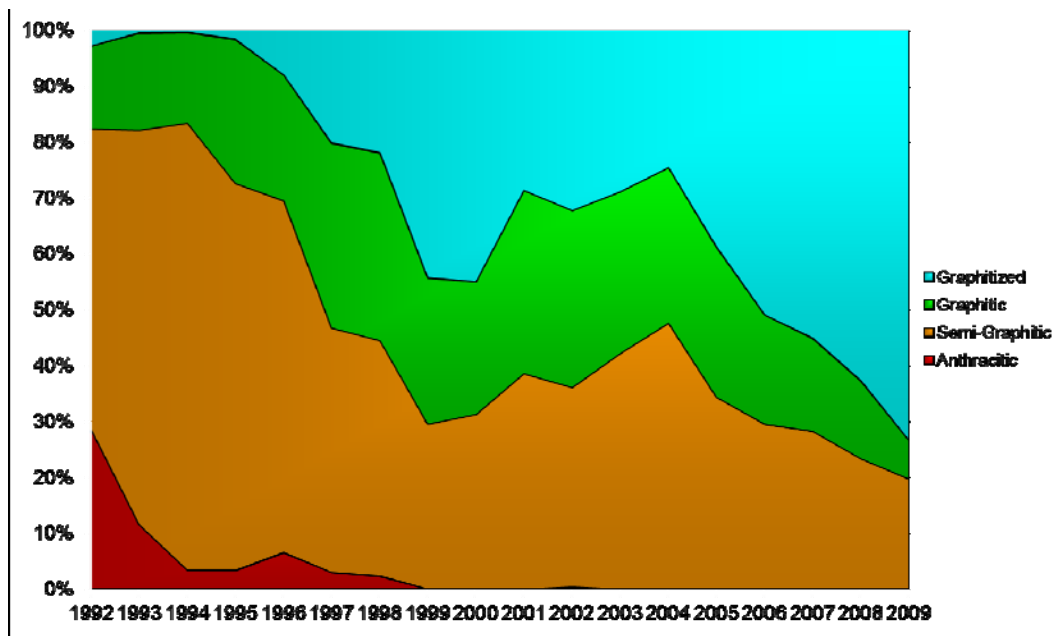


Figure 3. Sales distributions of different types of cathodes, with a significant decrease of the anthracitic (in red) and semi-graphitic cathodes (in orange), whereas the very conductive graphitized cathodes (in blue) became predominant.

3.2. Impact of copper inserts on the cathodes market

However, in the 1990's and 2000's, a significant change in the electrolysis design started to happen. Companies started to put in practice cells with copper collector bar inserts, which were invented many years earlier [2], but had not been in industrial use until the time when new ideas for industrial implementation came forth and were patented by various companies, such as Alcoa, Comalco, Alcan, BHP Billiton and Norsk Hydro [3, 4, 5, 6, 7]. Also, EGA and Hindalco have trialed collector bars with copper inserts in their electrolysis cells [8, 9].

There are different advantages to use copper in the collector bar. The first one is that, being more conductive than steel, copper decreases the cathodic voltage drop and by this way

decreases the specific energy consumption. Another advantage is that with a more conductive collector bar the current lines from the anode to the cathode block are more evenly spread over the length of the cathode block and are more vertical, which increases cell stability. Finally, the more even current lines over the length of the cathode blocks are expected to decrease the erosion rate. Consequently, despite the extra-cost of the copper insert, this kind of collector bars is now used widely by the aluminium smelters.

The impact of the copper insert is very significant on the voltage drop and has more impact than the cathode grade. The same as for the cathode grade changes, some care has to be taken to avoid too much heat loss through the cathode and collector bar. A balance between the low electrical resistance and the high heat loss has to be found.

It is also possible to use less conductive cathode and increase the copper content in the collector bar assembly, to reach the same voltage drop. This idea may have some interests because the more resistive cathode blocks are thermally more insulating. Some specific energy consumption gain may be found. And all the smelters are now trying to reduce their specific energy consumption and at the same time increase their daily production [8,10,11,12, 13]. With more copper in the collector bar and more resistive cathode, the current lines are also more even, which should stabilize the electrolysis cell even further. Finally, the highly conductive graphitized cathodes are the most sensitive to erosion. A move to more resistive cathode is also expected to decrease the erosion rate and increase the potlife.

For these reasons, in the recent years some aluminium smelters traditionally using graphitized cathodes have requested some graphitic cathodes for trial. And, contrary to all recent Greenfield projects, the THQ project in Vietnam was quoted for graphitic cathodes. Carbone Savoie estimates that the steady market of graphitic cathodes could increase from its usual 20 ktpy up 30 - 35 ktpy in the coming years, which is a significant increase. These estimates are presented in the Figure 4.

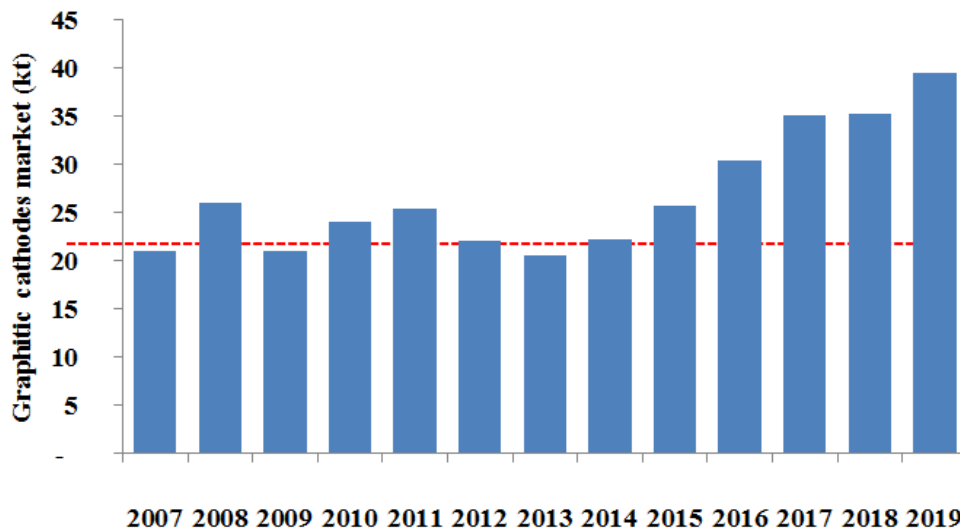


Figure 4. Based on Carbone Savoie internal data, this graph shows the market demand of graphitic cathodes for the past years and the estimates for the coming years, in thousand tons per year (ktpy).

4. Development of a New Cathode Grade

As described above, graphitic cathodes are mainly composed of synthetic graphite grains. These grains are either coming from recycling machining chips of graphitized cathodes, or from

graphitized electrode scraps. The quality of the graphite raw materials directly impacts the quality of the graphitic cathodes. With a graphitic cathodes market of 20 ktpy, the sourcing of good quality graphite is already difficult, and expensive. One can expect that with a 30 - 35 ktpy market, it will be more difficult to source good quality graphite, moreover at a reasonable price. Therefore, a deficit on the graphitic cathodes market or higher prices will be probable.

For these reasons, in 2012, Carbone Savoie (producing HC10, a graphitic cathode) decided to launch an R&D project to find a solution to produce these intermediate properties cathode. Carbone Savoie is producing both carbon and graphitized cathodes. This production is made on two separate production lines, except the baking which performed in the same workshop. It is then possible to adjust the balance between the two types of cathodes depending on the market fluctuation. Then it was possible to work with any raw material to produce this cathode.

Two kinds of carbon raw materials are available in big quantities, and at lower price than graphite raw material. The first is anthracite, but the graphitizability of this product is low. Whatever the HTT of anthracite, it will be less conductive than graphite. It is consequently not possible to use it as a replacer. The second one is petroleum coke. This product has a low conductivity when it is green but it is highly conductive after graphitization. Typically, the electrical resistivity of a graphitized cathode, based on petroleum coke, is 35 - 40 $\mu\Omega\text{m}$ before graphitization and decreases down to 8 - 10 $\mu\Omega\text{m}$ after graphitization.

4.1. Coke based cathode – laboratory trials

The idea was then to use the graphitization workshop to increase the HTT of a coke based cathode at a temperature such that the electrical resistivity will be around 20 $\mu\Omega\text{m}$. But in order to have the same production costs as HC10, the cost of this extra-step has to be compensated.

Some laboratory tests have been performed to determine the HTT which has to be reached. As shown in Figure 5, the product needs to be treated at about 2 300 °C to reach 20 $\mu\Omega\text{m}$. Such a temperature is not achievable with a conventional baking system. And definitely, a graphitization step is needed. During the graphitization, the cathode is heat treated by Joule effect, thanks to the current flowing directly into the cathode. The higher the energy, the higher the HTT, the lower the resistivity.

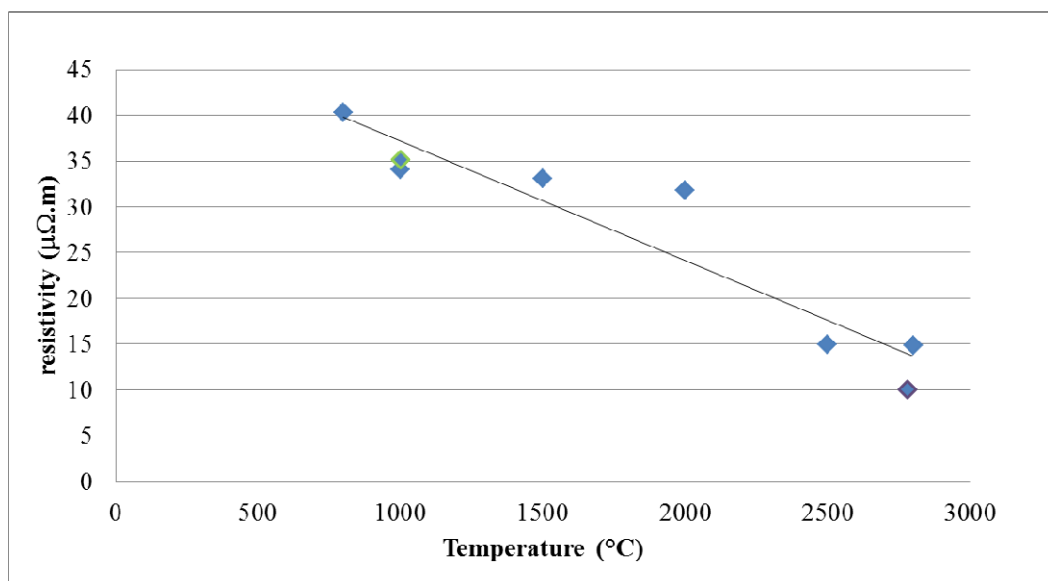


Figure 5. Resistivity of different samples, heat treated at different temperatures.

4.2. Coke based cathodes – industrial trials and properties

Once the temperature was determined, the next step consisted in an industrial test, to determine the input required to reach 2 300 °C. This was made in an industrial lengthwise graphitization furnace, usually dedicated to graphitized cathodes. A few graphitization batches were launched to determine accurately the input needed to get the same resistivity as graphitic cathodes.

Based on the energy reduction at the graphitization step, the lower price of the raw materials and small changes in the mix design, this trial cathode production costs are very close to the graphitic cathode production costs. Then, the trial cathodes were fully characterized. Their properties are summarized in the Table 2, compared to HC10, Carbone Savoie’s graphitic grade.

Table 2. Summary of the properties measured on the trial cathodes, compared to graphitic cathodes.

| CHARACTERISTICS | | Trial | HC10 |
|------------------------|---------------|-------|------|
| Apparent Density | | 1.65 | 1.60 |
| Ash Content | % | 1.0 | 1.0 |
| Flexural Strength | MPa | 12 | 9 |
| Electrical Resistivity | $\mu\Omega.m$ | 20 | 20 |
| Thermal Conductivity | W/m/K | 80 | 30 |

These properties measured at room temperature were comparable to those of the HC10. The electrical resistivity was on target. The density and the mechanical properties were higher. And the thermal conductivity was much higher for this product, but lower than graphitized cathodes, which is not detrimental for the use in electrolysis cell.

To complete this characterization, some measurements at high temperature were also made. The electrical resistivity and the thermal conductivity were measured simultaneously with the Kohlrausch method (this method has already been described previously) [14, 15]. The sodium absorption sensitivity has also been tested with Rapoport test. The values at high temperature are reported in the Table 3.

Table 3. Comparison of the properties measured for trial cathodes and typical HC10 values. The values in bold are measured at high temperature.

| CHARACTERISTICS | | Trial | HC10 |
|---|---------------|------------|------------|
| Apparent Density | | 1.65 | 1.60 |
| Ash Content | % | 1.0 | 1.0 |
| Flexural Strength | MPa | 12 | 9 |
| Electrical Resistivity | $\mu\Omega.m$ | 20 | 20 |
| Electrical Resistivity at 1 000 °C | | 13 | 15 |
| Thermal Conductivity | W/m/K | 80 | 30 |
| Thermal Conductivity at 1 000 °C | | 45 | 27 |
| Sodium Expanding Effect | % | 0.1 | 0.3 |

At 1 000 °C, the thermal conductivity of the trial cathodes has significantly decreased, down to 45 W/mK, and is closer to the graphitic cathode conductivity. The electrical resistivity is also significantly lower at 1 000 °C than at room temperature, decreasing from 20 to 13 $\mu\Omega.m$, being

also lower than graphitic cathode resistivity. Finally, the sodium sensitivity of the cathode is also lower.

This set of properties is acceptable and the target of having a cathode with the same electrical properties as a graphitic cathode not based on graphite raw material was achieved. For further development and discussion with aluminium smelters this trial grade was named Elit1.

4.3. Trials in industrial electrolysis cells

On the basis of these properties, Rio Tinto Aluminium accepted to try several cells lined with the Elite1 cathode. The electrolysis cells were started in 2014 at Rio Tinto Smelter in Jonquiere (Arvida), where the electrolysis cells are lined with graphitic cathodes. After two years, the cathode resistance, presented in Figure 6 shows that Elit1 has 9 % lower voltage drop than the graphitic blocks. The cells lined with Elit1 have also 2 % lower specific energy consumption.

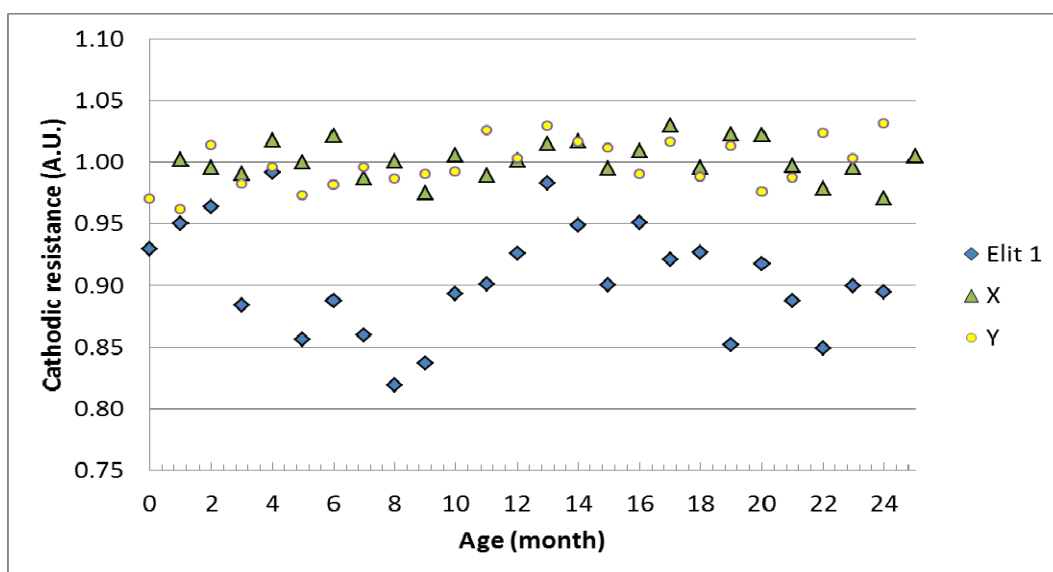


Figure 6. Cathode resistance of electrolysis cells versus age for Elit1 and cells with two different graphitic blocks (X and Y).

5. Conclusions

The market of cathode for aluminium electrolysis is slowly changing, adapting to the evolution of the aluminium smelting technologies. In the very recent years, an accrued interest for graphitic cathodes has been seen and a potential shortage for this kind of cathodes may be expected. In order to supply this market, Carbone Savoie initiated an R&D project in order not to be dependent on the graphite raw materials sourcing. The project ended successfully with the development of Elit1 cathode, having properties close to graphitic grades. After 2 years, the results of the industrial electrolysis cells lined with Elit1 cathodes look promising as these cathodes are performing better than the graphitic ones. Some other electrolysis cells of different cell technologies have been started with Elit1 cathode blocks.

6. Acknowledgement

The author wants to thank Rio Tinto Aluminium for its support in testing this new cathode and for data provided about the cathode performances in RTA electrolysis cells.

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