Ready-to-Use Cathodes in High-Amperage Technologies

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Abstract

The implementation of Ready-to-Use Cathodes (RuC®) using copper conductors in the cathodic system not only allowed to fully avoid rodding but also significantly decreased the specific energy consumption, reducing the carbon footprint of the Hall-Héroult process. The basic concepts, the cathode implementation, and the operating figures in smelting technologies ranging from 300 to 600 kA for up to 2.5 years of operation are highlighted. The robustness of the Ready-to-Use design is proven by stable low cathodic resistance allowing energy savings in the range from 0.15 kWh to 0.40 kWh per kg aluminum. An autopsy performed after 1140 days of operation revealed a fully intact copper bar system. Copper samples were taken from the bars at different locations and chemically analyzed, concluding that most of the copper value can be recovered after its useful life through recycling processes. Based on these positive results, further spread of the Ready-to-Use Cathode technology is expected.

Keywords

Copper • Collector bars • Productivity increase • Energy saving • Magneto-hydrodynamic • Cell design

Introduction

For the last two decades, the global electricity intensity of primary aluminium smelting has been reduced with average annual reductions of 1.2% from 2010 to 2017 [1]. In the case of old smelters designed 40 or 50 years ago, the measures taken to reduce energy have included among others, the use of prebaked anodes, multiple point feeding system, improved carbon anode designs, and control of heat losses via ventilation systems and compensation loops [2]. In addition, it has also become common to find energy reduction projects dealing with improvements in the lining design, increase of anode and cathode block dimensions, and cathode migrations (from semi-graphitic or graphitic to graphitized material). In the case of modern technologies, there has also been a development in the process control system, the use of compensation loops, as well as copper inserts in steel collector bars.

The use of copper inserts is becoming the standard cathodic solution in the aluminium industry. Retrofitting projects from Rio Tinto (APXe) [3], EGA (DX+, DX+ Ultra) [4], and Aditya Birla Science and Technology (Hin-dalco Mahan) [5], just to mention some of them, use copper inserts. With the correct design, it has proved to improve the horizontal current distribution in the metal, reduce cathode voltage drop (CVD) and pot voltage, and finally reduce the specific energy consumption per tonne of aluminium. Nevertheless, this cathodic solution follows the same principle of the steel bars in the sense that an additional cast iron rodding process is needed to connect the cathode block with the collector bars.

This extra step represents only additional work for the smelter. A careful control of the gradient and final preheating temperatures of the cathode block and collector bar as well as liquid cast iron with the correct chemical composition for flowability is needed for a successful rodding process without wing cracks. In addition, the rodding stations at many smelters are becoming older and high investments are

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needed for a retrofitting. Furthermore, handling liquid cast iron constitutes an intrinsic health and safety risk for the operators.

On the other hand, the next generation of cathodic solutions, the Ready-to-Use Cathode (RuC[®]) has been presented since 2016 [6]. The philosophy behind this concept is to avoid the costly and hazardous rodding process and to use copper conductors which offers advantages even compared to copper inserts in terms of lower pot voltage, lower energy consumption, lower noise level, increased current efficiency, longer lifetime, and can be easily recycled at the end of their useful life. Figure 1 illustrates examples of a cast iron-rodded copper-insert collector bar and an RuC[®] design.

RuC[®] is a flexible cathodic system, which allows for all smelting technologies an optimized design for thermal balance combined with an improved current distribution, improving the magnetic hydrodynamic (MHD) behavior of the cell, metal pad, and lower cathode voltage drop (CVD). Energy saving is a result of the lower pot voltage and improved current efficiency (CE), reducing the carbon footprint of the Hall-Héroult process. By energy saving and increased productivity the electrolysis process gets not only "greener" but also more economical. The fast and easy implementation supports the worldwide greenhouse emission reduction targets.

The RuC[®] stability in CVD with low electrical contact resistance is achieved despite the lower contact surface (60% reduction) compared to conventional cathodes. The low level and stable trend of CVD proves the robustness of the cathodic system.

Start-up procedures do not need to be modified when using RuC[®] but could even be shorter compared to conventional cathodes. Increased stability could be observed by faster stabilization in the early operation phase. Therefore, the pot voltage set point can be reached faster and at a lower level.

So far, more than 1300 RuC[®] blocks have been installed and started in 60 cells. This paper will present an update of high-amperage projects, operating in the range of 300 kA to 600 kA, all of which are targeting energy savings. RuC[®] is implemented in the most modern Western smelting technologies as well in the Chinese flagship technologies of NEUI. The reference cells and their performance could vary from paste-sealed steel bars to cast iron-rodded steel bars with copper inserts, as well graphitized cathode blocks or semi-graphitic grades.

The full copper recycling at the end of cell life constitutes a high residual value for the smelters. Several planned intermediate autopsies were conducted to validate the recycling value by an analysis of copper bars after 1.5 years and 3 years in operation. Metallurgical tests were performed on the collector bars and their integrity was confirmed. Less than 20 ppm additional impurities were found in the copper area close the surface of the bar, which allows the full recycling of copper in a standard and most valuable way.

Because of the high electrical conductivity of copper compared to steel and cast iron, RuC[®] needs much less metal volume inside the cathode block. The reduced metal volume is replaced by carbon cathode material which increases the distance from the collector bars to the cathode working surface. Compared to conventionally rodded cathodes, this provides 40–100 mm more wearable cathode material in height for erosion, which results in a longer cell life.

In addition, the improved magneto-hydrodynamic (MHD) cell state, resulting from lower horizontal current densities in the metal further leads to even longer cell life. The presented RuC[®] cells have been now operated for 30% to 50% of their standard cell life. In situ cathode surface profile measurements done by Lancelot[®] 3D measurement system [7] in 400 kA NEUI technology confirmed that, due to more uniform current distribution, RuC[®] average wear rate is 20% lower than for cathodes with standard collector bars.

RuC[®] Performance

400 kA and 600 kA NEUI Technology

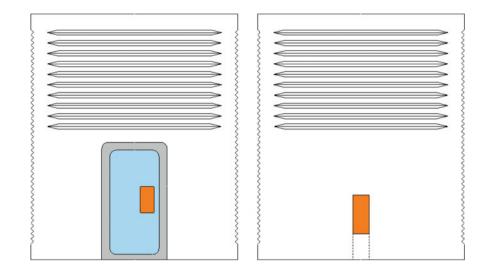
600 kA NEUI technology represents state-of-the-art aluminium reduction in China. Over the past years, not only the size and the amperage of Chinese electrolysis cells have been increased but also the productivity of the cells thanks to higher current densities.

In 2019, 400 kA NEUI cells were started with RuC[®] blocks. Reference cathodes were equipped with conventional cast iron-rodded steel bars. The target was to lower the cathode voltage drop (CVD) and achieve lower specific energy consumption (SEC). Cell life was also expected to be longer thanks to lower maximum current density at the cathode surface (more uniform electrochemical wear) and larger carbon height on top of the collector bars (+85 mm). Besides the cathode upgrade, the lining was modified to enhance the thermal insulation of the cells for maintaining a good thermal balance of the cell at lower internal heat generation.

These trial cells are now more than 800 days old, and their performance can be assessed profoundly. Thanks to the use of copper bars, the effective section of the collector bars is increased, and the CVD is significantly reduced $(-98 \text{ mV})^1$ see also Fig. 2). The CVD evolution is stable and

¹ All time averages of performance indicators exclude the first 90 days of operation.

Fig. 1 Copper-insert collector bar design example (left) showing the cast iron (gray), steel bar (blue) and copper insert (orange), and typical RuC[®] design (right) (Color figure online)



the increase over time is lower for the RuC[®] cells compared to the reference cells.

The heat losses of the RuC[®] cells are slightly reduced as mirrored in the lower cell voltage (-23 mV, see also Fig. 3). Thanks to the lower CVD, the anode-to-cathode distance (ACD) is increased and in combination with the enhanced current distribution in the cell, the magneto-hydrodynamic (MHD) stability of the RuC[®] cells is improved yielding a higher current efficiency (CE) (+1.1%). As a result, the SEC is decreased by 0.26 kWh/kg as shown in Fig. 4.

Based on the early results of the 400 kA cells, new RuC[®] and lining designs were developed for the 600 kA NEUI technology with the target to maximize the SEC savings. Additional modelling tools and resources were engaged to better predict the cell performance. In 2020, trial cells were started in a 600 kA line. After 300 days of operation, the normalization period is over, and the performance of the cells is promising.

The CVD is decreased by design but not to the same extent as for the 400 kA cells. As shown in Fig. 5, the difference in CVD is -55 mV. The total heat losses, however, are more significantly reduced as indicated by the evolution of the cell voltage (see Fig. 6). The difference to the reference cells is -72 mV. In terms of heat losses, RuC[®] cathode design is as important as the lining design and an optimum must be found between low CVD (ACD margin) and low heat losses.

The cell voltage savings for the RuC[®] cells are larger than the CVD decrease alone which is a direct result of the lower ACD. Despite this ACD decrease, the current distribution in the cell is improved versus reference cells in such a way that the CE is increased as for the 400 kA cells (+1.1%) which is a direct consequence of the highly conductive copper bars creating a more homogeneous cathode current distribution. It is noteworthy that anodic and cathodic current densities are higher for the 600 kA cells compared to the 400 kA cells,

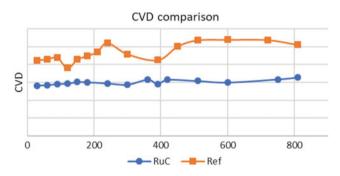


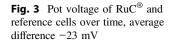
Fig. 2 CVD of $RuC^{(B)}$ and reference cells over time, average difference -98 mV

making the benefit of RuC^{\otimes} on the MHD state of the cells more sensitive.

Thus, thanks to the lower cell voltage and higher CE, the SEC is significantly reduced as shown in Fig. 7 (-0.39 kWh/kg). This result confirms the potential of RuC[®] in terms of performance for the 600 kA NEUI cell and adds up to the other benefits that are the longer cell life (more uniform erosion, +70 mm carbon height) and the recyclability of the copper bars.

330 kA Technology

In year 2019, RuC[®] cells were also implemented in a 330 kA line. These cells have a similar design compared to the ones using 400 kA NEUI technology. The interesting feature lies in the continuous CVD data over close to 800 days which confirms the trend observed for the 400 kA and 600 kA NEUI cells. As shown in Fig. 8, the CVD is significantly reduced (-116 mV) whereas the heat losses are decreased but to a lesser extent (-56 mV, see Fig. 9). The evolution of CVD is stable and the increase over time is lower than for the reference cells. This demonstrates that the evolution of



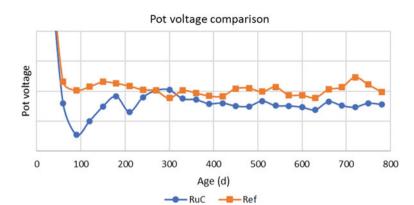


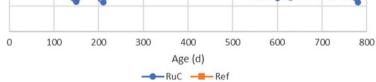
Fig. 4 SEC of RuC[®] and reference cells over time, average difference -0.26 kWh/kg

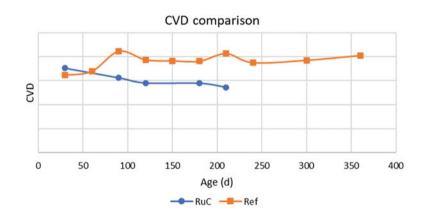
Fig. 5 CVD of RuC[®] and reference cells over time, average difference -55 mV

Fig. 6 Pot voltage of RuC^{\circledast} and reference cells over time, average difference -72 mV



SEC





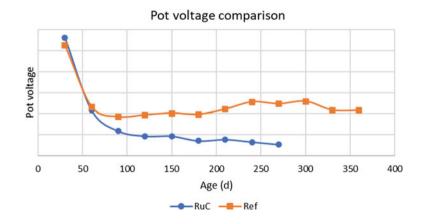
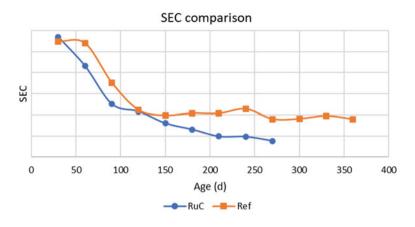


Fig. 7 SEC of $RuC^{\textcircled{8}}$ and reference cells over time, average difference -0.39 kWh/kg



the electrical contact resistance of the small copper bars inside the cathode is better than for the large cast iron-rodded steel bars.

For the same reasons as mentioned earlier (larger ACD, enhanced current distribution), the cell MHD stability is improved, and the CE is positively impacted (+0.7%). All in all, the SEC of the RuC[®] cells is decreased by 0.27 kWh/kg in average after 800 days of operation (Fig. 10).

400 kA Technology

This last example is to show that RuC[®] is not specific to any technology and that it can be adapted to any cell, building up on the existing design to improve the cell performance. In the present case, the reference cathode uses cast iron-rodded steel bars with copper inserts. The cell lining design remained untouched and only the cathode blocks were replaced with RuC[®] blocks. The cells were put in operation in 2019 and cell performance over 700 days of operation is presented.

The CVD changed only slightly (-25 mV, see Fig. 11) but heat losses and hence cell voltage are significantly reduced (-115 mV, see Fig. 12). Of course, the lower heat losses must provide the same heat balance at bath and metal level to keep the same ledge protection. It is important to remind that heat losses are not only determined by the cell thermal resistance but are also influenced by MHD parameters such as metal velocity (convection), metal level (lower with improved MHD), metal upheaval (ledge shape), or cell instabilities (beam movements, anode cover integrity). Thus, the enhanced MHD state of the RuC[®] cells contributes to lower cell voltage.

Copper Analysis

A metallurgical analysis of copper samples was performed after more than 800 days in use in RuC[®] blocks. Figure 13 shows the copper cross section (polished) and three spots of analysis. Copper content and impurities were determined by glow discharge optical emission spectroscopy (GDOES) on these positions. All measured spots have shown copper contents above 99% with minor increase of impurities compared to the original material used. Given this high copper purity, the metal recycling companies can use standard recycling process and pay LME Cu for each kg minus a recycling fee, which ends up above 90% of LME as cash return.

Cell Modelling

As mentioned earlier, modeling tools are used to predict the behavior and performance of the RuC[®] cathodes within the electrolysis cell, and thus help finding the optimum design. Each RuC[®] design is customized and may evolve over time depending on the smelter objectives and/or constraints. In Sect. "RuC[®] Performance", the impact of the cathode on the cell MHD state was analyzed to explain the performance of RuC[®] cells. Some computational results illustrate these effects.

The 3D full cell models of a reference cell and of a RuC[®] cell have been computed for a 240 kA cell technology. The Thermal-Electrical-MHD problem, accounting for the neighboring cells and lines, is solved. The reference cell is using cast iron-rodded steel bars with copper inserts and the

CVD (mV)

0

Pot Voltage (V)

0

SEC (kWh/kg)

0

Fig. 8 CVD of RuC[®] and reference cells over time, average difference -116 mV

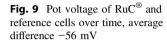
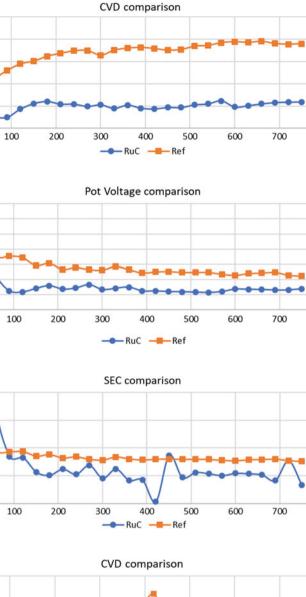
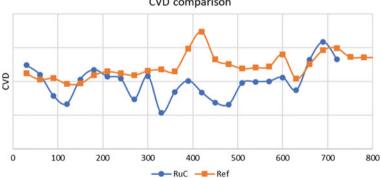


Fig. 10 SEC of RuC^{\circledast} and reference cells over time, average difference -0.27 kWh/kg

Fig. 11 CVD of RuC^{\circledast} and reference cells over time, average difference $-25\ mV$





RuC[®] cell lining is unchanged. The CVD is decreased by 21 mV and the cell voltage by 56 mV. Figure 14 shows the current density in the liquid metal for both the reference cell and the RuC[®] cell. The horizontal component and the maximum value of the current density are lower for the

RuC[®] cell which are the result of a more uniform current density at the cathode surface.

The current density and, in particular, its horizontal component are important for the magnetic forces and affect the metal velocity and metal upheaval as shown in Figs. 15

800

800

800

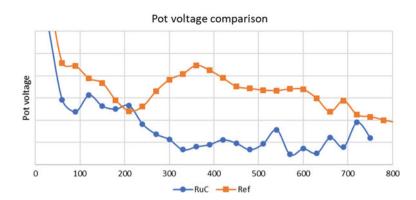




Fig. 13 Copper analysis after 800 days in operation, measurement positions

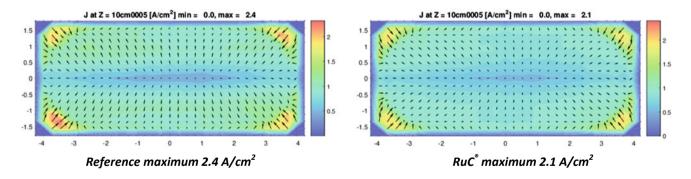


Fig. 14 Current density in A/cm² in the liquid metal, module with color map, and horizontal component with arrow plot

and 16. Maximum velocity and upheaval values are larger for the reference cell. A higher metal velocity means stronger convection and thus enhanced heat losses. It also correlates with larger instabilities and CE losses. Likewise, higher metal upheaval leads to less uniform heat fluxes on the cell long sides resulting in less uniform ledge shape which is detrimental to cell life and favors instabilities.

Conclusions

The operation of more than 1300 RuC[®] cathode blocks in 60 cells and data for more than 800 days of operation confirm that the aluminum industry has a new solution at hand to minimize its carbon footprint. Indeed, a reduction of 0.3 kWh/kg represents a worldwide saving of 19 500 GWh/year

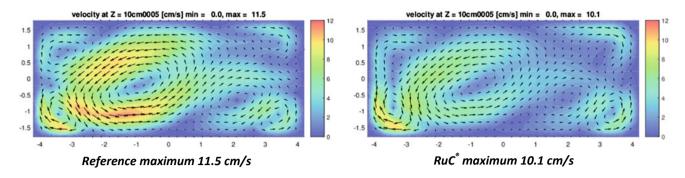


Fig. 15 Velocity in cm/s in the liquid metal, module with color map, and horizontal component with arrow plot

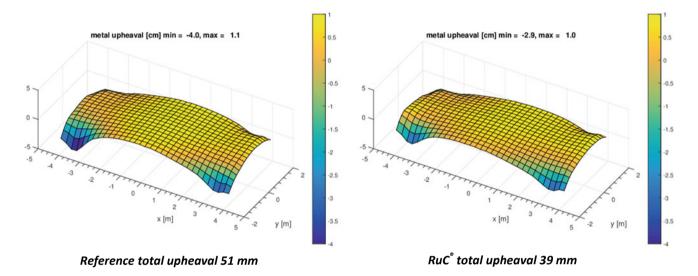


Fig. 16 Metal upheaval in cm

or 2.2 GW power (for 65 million tonnes of aluminum produced per year).

RuC[®] demonstrated a stable CVD performance in high-amperage cells with significant energy saving of 0.2 kWh/kg to 0.5 kWh/kg and with high residual value on the copper bars after their useful life.

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