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Ready-to-Use Cathodes for the Hall-Héroult Process

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Abstract

Ready-to-Use Cathode (RuC®) blocks based on the use of copper inside the cathode have been implemented in many aluminum smelters since 2015. The concept and key performance parameters are presented, along with measurements of cathode resistance, collector bars current distributions and temperature at cell start-up and as function of cell age. Today more than 500 RuC® cathodes are in operation and more RuC® cells are started every day. Significant energy savings and improvement of the cell magneto-hydrodynamic state are achieved. The reduction of the maximum cathode surface current density should lead to longer cathode life. The concept allows the avoidance of cast iron rodding and recovery of copper at the relining time. A new generation of cathode is ready to be implemented.

Introduction

The concept of Ready-to-Use Cathode or RuC® has been presented at TMS 2016 [1]. It consists of avoiding the rodding process and using copper giving a number of advantages.

RuC® is a cathode solution without any rodding process at smelter site and giving customer benefits in energy and cost saving, productivity, lifetime and high value in copper recycling. RuC® cathodes are delivered ready for installation into the pot shell. The iron casting rodding process constitutes a high health and safety risk in many smelters, working with liquid cast iron over 1’300 °C. This risk is completely eliminated by RuC®. The assembly of Cu bars is done at COBEX plant site just by mechanical means and without any casting process. The connectivity of cathode bars to bus bar system via flexes is not changed and adapted to each smelter standards and specifics. Precise machining of cathode block combined with high accuracy of metal parts are the keys for good electrical contact and CVD performance. Because of the high electrical conductivity of copper compared to steel and cast iron, RuC® needs much less metal volume inside the cathode block. This reduced metal volume is replaced by carbon cathode material which increases the distance from the collector bars to the cathode working surface (liquid aluminium). Compared to conventionally rodded cathodes, this provides 40 mm to 100 mm more wearable cathode material in height for cathode erosion. Figure 1 is showing a conventional Cu insert design and a typical RuC® design. The lower amount of metal volume is clearly visible as well as the additional cathode material for erosion.

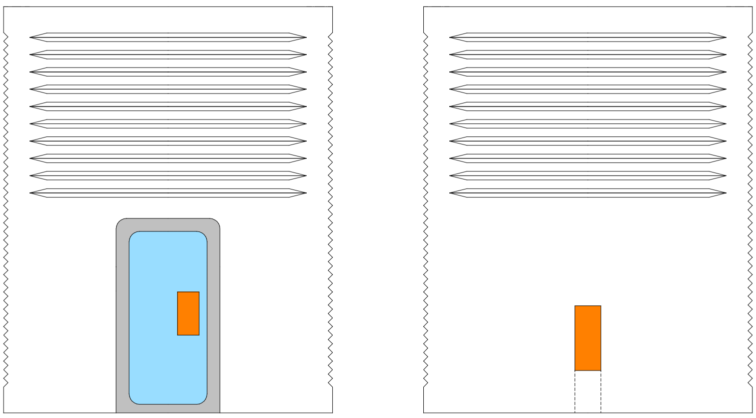

Figure 1: Cu insert design versus typical RuC® design

When the CVD is lowered, the heat loss of the cell should also be reduced to take advantage of the lower

CVD and hence to save energy. Even with only a 30% contact surface between metal and cathode blocks RuC® cathodes show the same CVD trend as iron casted Cu-inserted steel bars. Material robustness and excellent electrical contact resistance of the RuC® system is demonstrated.

A longer cell life is therefore expected. Under a linear assumption of erosion, the cell life extension should be between 1.5 and 3 years. In addition, the improved magneto-hydrodynamic cell state resulting from lower horizontal current densities should lead to even longer cell life. Indeed, most of the erosion is attributed to high local current densities leading to electro-chemical wear phenomena. A more even horizontal current distribution is achieved by RuC® by lowering the current density peak at the outer end of the cathode often observed in different technologies [2]. The amount of copper and collector bars design determine the performance of RuC®. The design is optimized for each cell technology and smelter.

The global impacts of RuC® are lower cell noise, increased current efficiency, lower specific energy, lower specific cost and potentially higher productivity. All is related to the use of copper in an appropriate way.

The electrical resistance of the RuC® cathodes is designed and optimized to the needs of the smelting technology and smelter strategy. Starting from a cathode resistance reference, whilst maintaining the thermal balance, up to 100 mV CVD reduction were achieved.

Energy savings are driven by lower voltage drops in the cathode assembly, higher CE and lower Anode-to-Cathode Distance (ACD) due to the improved cell magneto-hydrodynamic stability. Best results from RuC® may require minor cell design improvements and/or start-up procedure upgrade. Necessary cell lining and start-up changes for energy saving projects with RuC® are supplied to the smelters together with RuC® cathode blocks. Technical services and RuC® product to smelters are supplied worldwide. RuC® projects are managed from start, over design phase, installation until early start-up and regular performance monitoring is assured. Advanced modelling tools are used for the cell optimization.

Compared to conventional steel bars or copper inserted bars, RuC® has much higher economic value for the smelters. Recovery of copper is easy at the end of the cell life, energy saving, current efficiency and cell life are the main drivers.

Seen from the outside, the RuC® assembly looks very similar to the conventional cathode after casting. Figure 2 shows one example. Cathode block dimensions are the same, steel bars cross section through the shell window and the connection to the existing flexibles are unchanged. RuC® is available in all cathode block material grades from amorphous over graphitic to graphitized.

Figure 2: RuC® cathodes ready to be shipped

The oldest RuC® was 3.5 years in operation and stopped for a planned autopsy to analyze the copper condition and collector bars deformations. The development of RUC® was driven by implementation of many blocks in a short time and planned intermediate autopsies in periods of 1 to 4 years. Intensive monitoring and analysis were done to keep the improvement cycles short and implementation as fast as possible. Two years after the first trials, a new generation of RuC® removing all potential weak points was developed and reliable cathode systems were brought to the market.

Measurements

This paper is summarizing the results from more than 500 RuC® cathodes which are in operation in seven countries, in smelting technologies ranging from 100 kA to 600 kA.

The validation process consisted of evaluating the evolution of the cathode resistance, the collector bars current distribution, the collector bars end temperature and determining the cell magneto-hydrodynamic stability. Reference cells using standard steel bars or copper inserted bars rodded with cast iron were considered for benchmarking technical and economic data. Both gas and electrical preheating have been used for cell start-up. The cathode resistance was determined for each cathode block by measuring the collector bars current using a DC clamp measurement device with ±2% accuracy and by measuring the voltage from the liquid metal to every collector bar end using a CV-Therm measurement device assuring an accuracy of ±1%. A measurement system analysis (MSA) was carried out for cathode resistance based on CVD and current measurements with 2 operators, to check the capability of the system. Result of MSA is a detectable difference of 0.6 µΩ in a value range of 33 – 43 µΩ for one cathode connection (half or quarter of cathode), which corresponds to a detectable CVD difference of 2 mV and 81 A in current.

A number of cases are presented to demonstrate RuC® performance .

Case 1: Cell at 110 kA

This RuC® cell is operating at a low amperage but at an anodic current density above 0.8 A/cm². Figure 3 is showing the average CVD saving of RuC® cell versus reference cells during the first 450 days of operation. An average CVD saving of 93 mV is achieved after 450 days of operation. The reference group is made of 6 cells with cast iron rodded steel bars. All blocks (reference and RuC®) are 100% graphitic.

Figure 4 shows the cell voltage saving and CVD saving during the same period. Energy saving with RuC® varies in a range from 0.15 kWh/kg up to 0.25 kWh/kg. The cell voltage saving is lower than the CVD saving meaning that the ACD is larger for the RuC® cell. In this case, it is possible to further optimize the RuC® design in order to maximize the cell voltage saving.

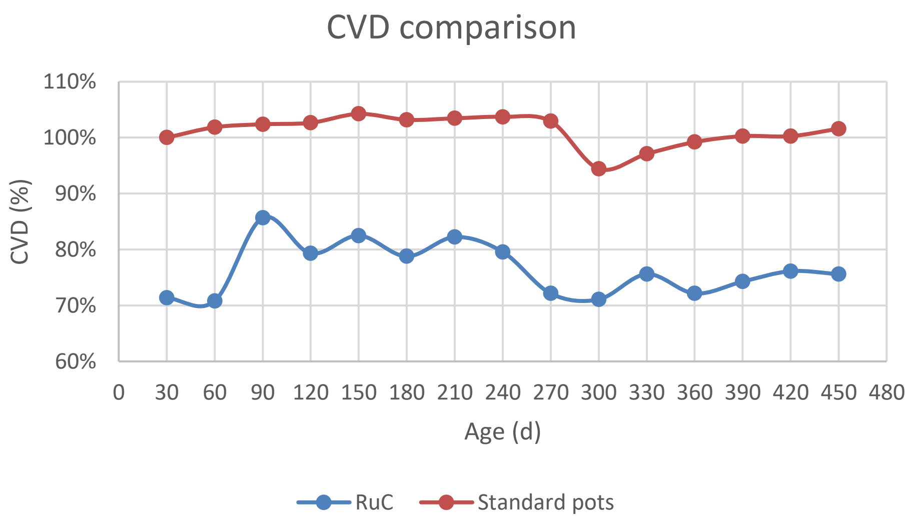

Figure 3: CVD results of RuC® cell versus reference cells after 450 days

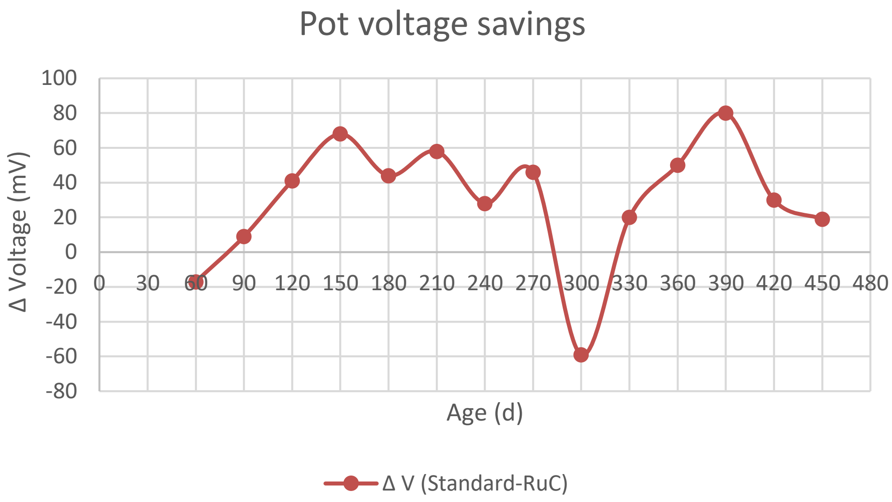

Figure 4: Cell voltage savings of RuC® cell versus reference cells during first 450 days of operation

Figures 5 and 6 show the collector bars current distribution (CCD) of a RuC® cell and of a reference cell, setting the calculated average current pick-up per collector bar to 100 %. The RuC® cell CCD is more uniform and with less variation compared to the one of the reference cell.

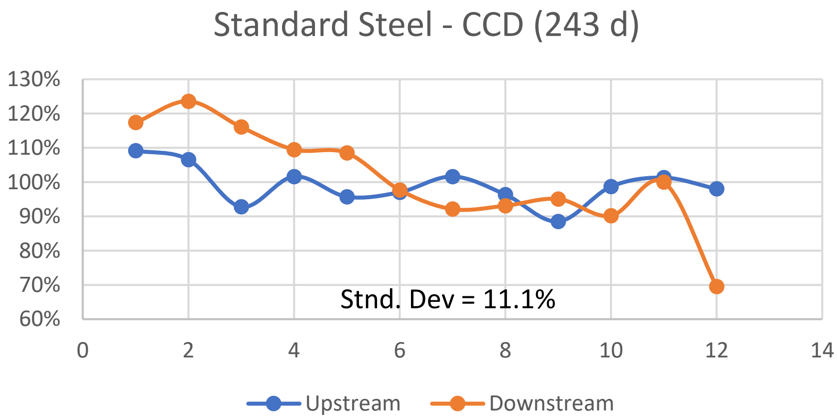

Figure 5: CCD of a reference cell after 243 days

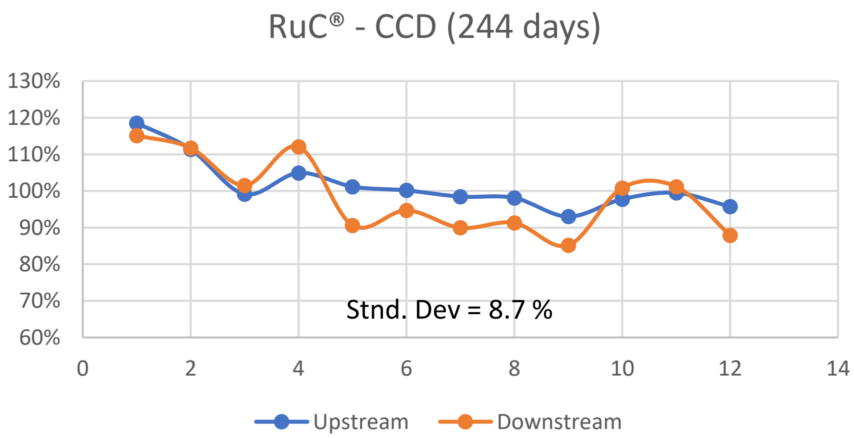

Figure 6: CCD of RuC® cell after 244 days

Case 2: Cell at 125 kA

Table 1 shows the average cell noise, cell voltage and current efficiency (CE) for four reference cells with steel collector bars and four RuC® cells after 150 days.

Table 1: Average noise, cell voltage and current efficiency for 4 reference cells and 4 RuC® cells

Pot age days	**Avg Ref (4 pots)** Noise μΩ	CE %	**Avg RuC (4 pots)** Noise μΩ	CE %	**Δ Pot V** (Ref-RuC) mV
1-30	2.29	89.9	2.62	89.8	85
31-60	3.21	90.3	2.45	90.0	55
61-90	2.58	90.3	2.44	90.3	10
91-120	2.90	90.5	2.66	87.5	50
121-150	4.57	88.4	3.35	89.7	48
Avg 31-150	**3.45**	**89.9**	**2.73**	**89.4**	**41**

The cell voltage is 41 mV lower for the RuC® cell. The CE is slightly lower despite lower noise level. Due to the accuracy of the tapping method a longer evaluation period is needed to determine the CE.

Case 3: Cell at 185 kA

Figure 7 shows the evolution of the cathode resistance over the first 150 days of operation. The cathode grade is 100% graphitic.

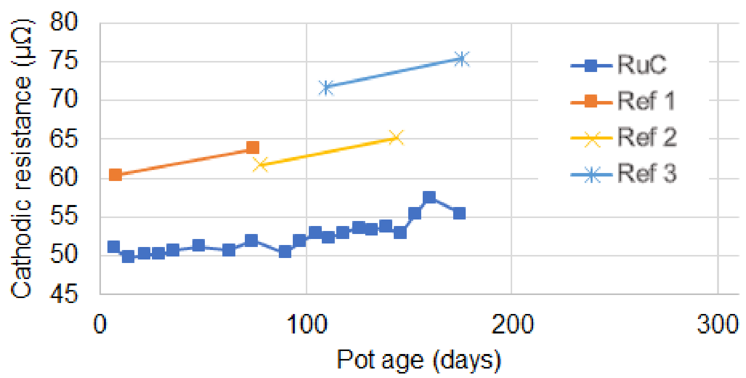

Figure 7: Cathode resistance for reference cells and for a RuC® cell

Figures 8 and 9 show the collector bars current distributions after 32 days and after 154 days of operation. The distributions are smooth and stable over time. The variations are mainly due to the busbars system.

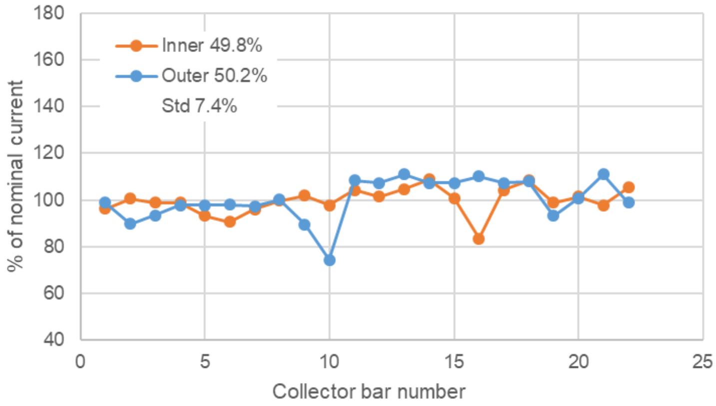

Figure 8: Collector bars current distribution after 32 days

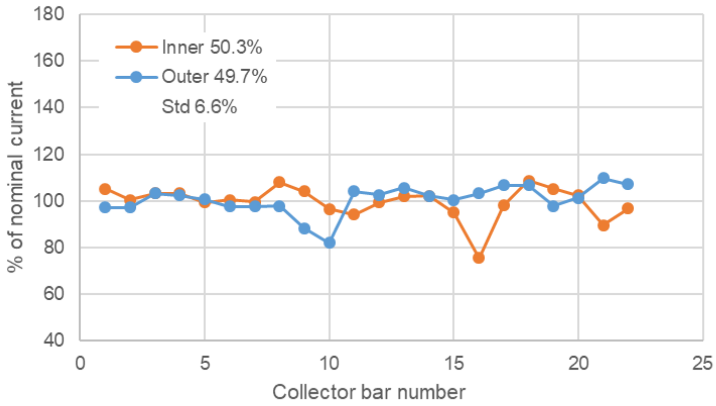

Figure 9: Collector bars current distribution after 154 days

Table 2 shows cell voltage and cell noise averaged over 5 months of operation for steel collector bars cells, Cu inserts cells and a RuC® cell. Cell voltage is 30 mV lower for Cu inserts cells and 60 mV lower for the RuC® cell. CVD is lower for RuC® cell compared to Cu inserts cells and standard steel cells. The difference between the CVD saving and the cell voltage saving represents an increase of ACD which is beneficial to the cell stability. Cell noise reflects this enhanced cell stability due, one the one hand, to the increased ACD and, on the other hand, to the improved current distribution in the liquid metal.

Table 2: Average cell voltage saving and cell noise over 5 months period for steel collector bars, Cu inserts and RuC® cells

Avg Steel bar (4 pots)			**Avg Cu-Inserts (5 pots)**			**Avg RuC (1 pot)**		
Pot age days	Noise µΩ	Cell voltage V	Pot age days	Noise µΩ	Cell voltage ΔmV	Pot age days	Noise µΩ	Cell voltage ΔmV
627-909	**0.128**	**Reference**	**91-373**	**0.115**	**-30**	**31-160**	**0.108**	**-60**

Case 4: Cell at 220 kA

Figure 10 is showing the relative cathode resistance for a reference cell (with copper-insert collector bars) and for RuC® cathodes over 500 days for graphitized blocks. Both resistances are normalized against the resistance of each at day 1. It shows that the resistance variations over time are 100% similar and are most likely due to process variations (current change in the line, bath temperature, cathode aging, operation, etc.).

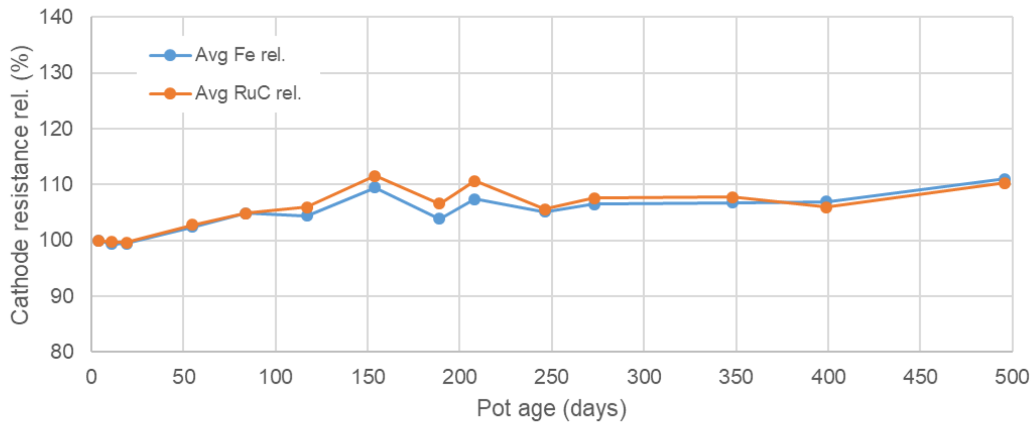

Figure 10: Relative cathode resistance for a reference cell and for RuC® cathodes

The evolution of the average temperature at the collector bars end is shown in Figure 11. Again, temperatures are following very similar fluctuations although the RuC® cathodes lead to a slightly lower bar end temperature. This can be explained by the collector bar design itself. The CVD was designed to reflect the existing CVD for the same lining, in order to keep the thermal balance at the same level.

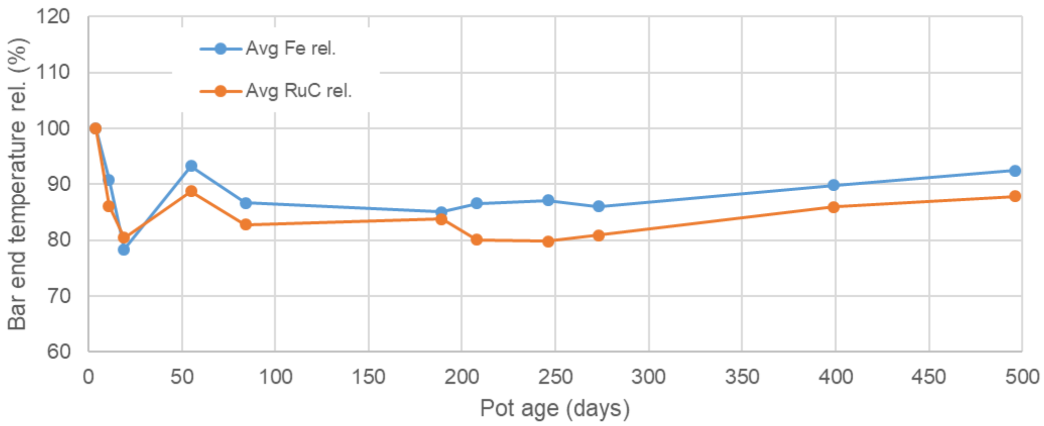

Figure 11: Evolution of the average temperature at the collector bars end

Case 5: Cell at 330 kA

Two RuC® cells are operated in a 330 kA technology. Reference cells have conventional steel collector bars. Average cathode resistance and cell voltage are reported over the first 100 days of operation. After the stabilization period, the CVD is more than 110 mV lower and cell voltage is 85 mV lower with the RuC® design (Table 3). The cell key performance indicators will be closely followed up to confirm the initial good performance.

Table 3: Cathode resistance and cell voltage after 90 days period for reference cells and two RuC® cells

Pot age days	Δ Pot V (Ref-RuC) mV	Δ Cath. resistance (Ref-RuC) μΩ
1-30	157	0.32
31-60	59	0.32
61-90	85	0.34
Avg 31-90	**72**	**0.33**

Case 6: Cell at 400 kA

The next RuC® cell is operated in a 400 kA technology. It is compared to two reference cells with similar age (Figure 12). Reference cells have steel collector bars and amorphous, 50 % graphite-added blocks. RuC® cathode block material is graphitized. This transformation of semi-graphitic to graphitized was done simultaneously with RuC® implementation. The cell lining was adapted to keep the thermal balance, especially for cathode block material change, and to convert the CVD saving into cell voltage saving.

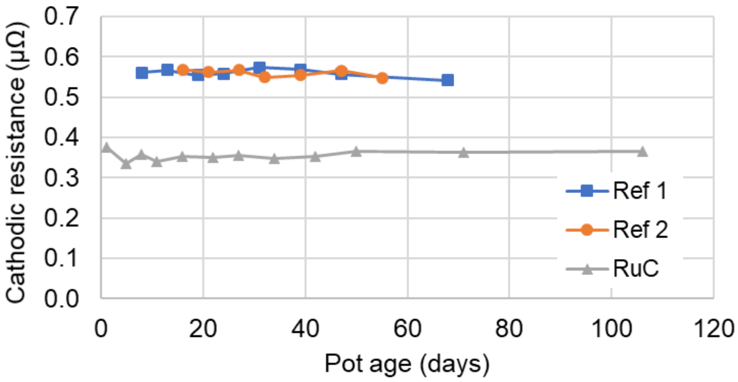

Figure 12: Cathode resistance of RuC® cell versus two reference cells (steel collector bars)

The CVD saving is significant (80 mV) and stable over the first 100 days of operation. As reported in Table 4, the cell voltage saving is around 60 mV meaning that the ACD was increased by a distance equivalent to 20 mV.

Table 4: Average bath temperature, cell voltage and current efficiency (CE) after 100 days period for two reference cells and one RuC® cell

Pot age days	**Avg Ref (2 pots)**		**Avg RuC (1 pot)**		**Δ Pot V (Ref-RuC)**
	T bath °C	CE %	T bath °C	CE %	mV
1-25	976	85.1	975	97.6	-35
26-50	969	88.7	971	87.7	16
51-75	971	89.3	964	91.1	68
76-100	971	88.9	968	90.4	56
Avg 51-100	**971**	**89.1**	**966**	**90.8**	**62**

Figures 13 shows that the collector bars nominal current distribution is stable over time but variation and asymmetry due to the busbars design are affected by the much lower cathode resistance. Nevertheless, the current efficiency is improved by 1.7% for the RuC® cell after 100 days (Table 3).

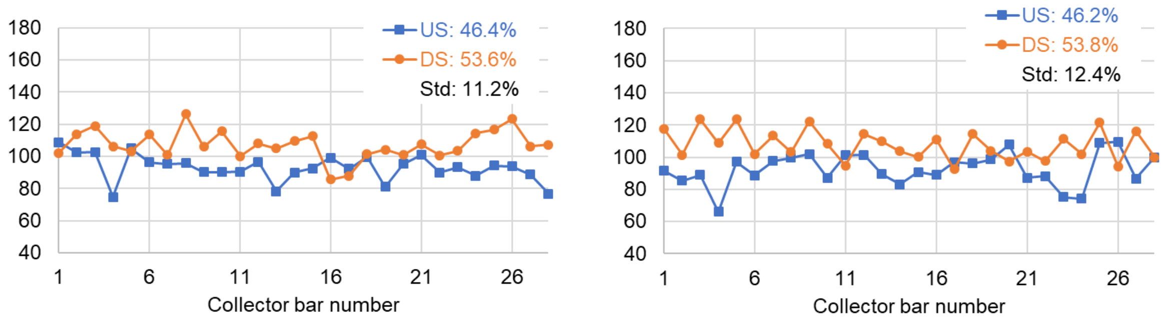

Figure 13: Collector bars nominal current distributions after 1 day and 100 days for RuC® cell

The specific energy saving is 0.45 kWh/kg for the period of 51 to 100 days after start-up. The overall target is 0.70 kWh/kg reduction in specific energy consumption. A second cell will be installed soon with improved lining and RuC® designs in order to maximize cell voltage saving.

Conclusions

Data from 6 different smelters and different technologies confirm the material stability and robustness of RuC® over time. A minimum reduction of 50 mV of CVD was achieved in all smelters. The energy saving varies significantly depending on the level of lining change and on the type of technology. Indeed, when the magnetic compensation is poor, the impact of the copper bars is larger than for a fully optimized technology. In all cases the height of carbon above the RuC® collector bars is much higher and longer cell life is expected to be demonstrated soon. Due to the specific energy consumption reduction, current efficiency increase, cell life increase and relining cost reduction, the RuC® solution demonstrates lower metal production costs.

References

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2. S. Das et al., *Journal of Metals* 2014, 235-244