COPPER BARS FOR THE HALL-HÉROULT PROCESS

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Abstract

The use of copper inserts in steel collector bars has proven to be an efficient way of improving the Hall-Héroult process. It helps at decreasing the specific energy consumption and improving the cell productivity. A further step is presented for which only copper is used inside the carbon cathode. The feasibility was modeled, tested at laboratory scale and measured in a real cell. The issues, advantages and potential of using 100% copper bars as current collectors inside the carbon blocks are discussed. Modeling results are validated by measurements.

Introduction

Copper has been proposed for many decades for improving the Hall-Héroult process [1]. A number of patent publications have proposed different approaches for minimizing the voltage drop from the liquid metal to the end of the collector bars. The idea is to use a high conductive material as a complement to the existing steel collector. A number of patents disclose solutions using copper inserts inside steel collector bars. Reference [2] splits the cathode and the collector bars in sections. Reference [3] uses high conductive materials inside the collector bars. References [4, 5] present the use of copper in combination with steel collector bars. Today there are a number of smelters using copper inserts in the collector bars but none report about the actual results as it can give a real competitive advantage.

On the one hand copper helps at decreasing the cathode voltage drop (CVD) and on the other hand it helps at improving the cell magneto-hydrodynamic (MHD) state. If copper has not made a breakthrough up until recently, it must be mainly linked to the misunderstanding on the global thermal-magneto-hydrodynamic effects. Indeed, copper must be designed to decrease the CVD but also to realize the right heat extraction through the collector bars, the right isotherms in the cathode and the right current density in the liquid metal. Therefore the full thermal-electrical and magneto-hydrodynamic effects must be analysed. A correctly designed cathode leads to significant advantages [6]. In order to achieve the desired current distribution in the liquid metal, collector bars must be electrically insulated on some areas. The insulated areas not only depend on the collector bars parameters such as height, width, length but also on the cathode dimensions and properties. The other important parameter is the pressure between collector bar and carbon block at operating temperature. The combination of all factors makes it impossible to design a solution without referring to modeling work. One way of decreasing the complexity of using copper inserts with their various designs is to consider only copper inside the cathode [7]. Copper is chemically stable with carbon and its melting point is 1085°C. Copper inserts are usually imbeded in the steel bars which are further implemented in the carbon cathode by casting cast iron around them. This requires the productionof liquid cast iron and i pre-heating the cathode before pouring the cast iron. Furthermore, at the end of the cell life, it becomes very difficult to recover the valuable copper as it is fused together with the steel bar. The authors have studied a solution that should remove the costly operation of casting in the steel bars using cast iron, and that would allow recovery of at least e95% of the copper. So how could we remove the need for cast iron and stop the fusion of copper with the steel bar?

The concept is patented [7] and consists in using only copper inside the cathode and couple the copper bar to a steel bar outside the cathode. One can not use copper over the full length as the temperature would be too high at the end of the bar. It would not be possible to connect the copper to the aluminium flexes and heat losses would be too high.

This paper presents the approach to validate the concept. There were many open questions and following had to be answered:

- what is the contact resistance between copper and carbon in operation conditions?
- will copper melt inside the carbon block if the liquid aluminium in the cell will reach 1100 °C?
- where and how should the copper bar connect to the steel bar?
- what is the CVD when using a copper bar?

In order to answer these questions tests were performed with small samples in a laboratory at room temperature and up to 900°C. A test was performed in a real electrolysis cell with in situ measurements. All experiments were supported by modeling work to predict the electrical potential and temperature fields.

Laboratory tests

Figure 1 shows a sample of graphite cathode that was used to evaluate the electrical contact resistance between copper and carbon as function of the temperature, pressure and surface conditions.

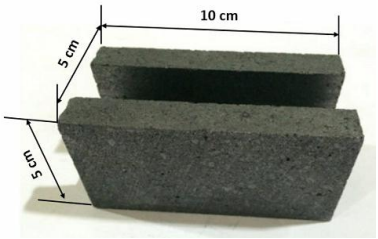

Figure 1: Graphite cathode sample

To be as close as possible to the situation existing in the cell, the

sample was heated at 900°C before performing measurements. Figure 2 shows the box used to heat the sample at 900°C. The sample was covered with coke granules to create a reducing atmosphere.

Figure 2: Box at 900°C containing the sample

Figure 3 shows one carbon sample together with a copper element at 800°C. A current of 10 amperes was injected at one end leading to a current density of 1 A/cm^2 between the copper element and the carbon sample. The voltage was measured simultaneously. The comparaison of measurement to modeling results allows to determine the electrical contact resistance.

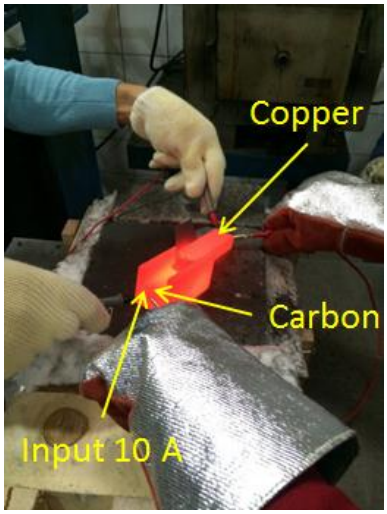

Figure 3: Carbon sample and copper at 800°C

A second experiment consisted in registering the voltage over time while heating the sample from room temperature to 900°C. Figure 4 shows where the electrical potential was recorded during the heating process at four different locations (A, B, C, D).

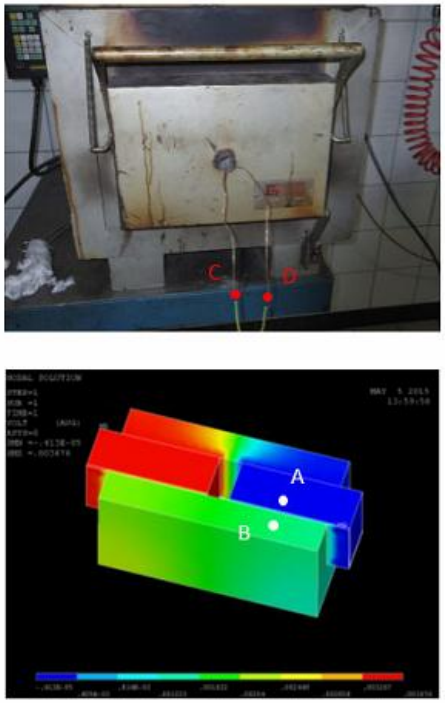

Figure 4: Measurement locations of the electrical potential

Figure 5 shows the voltage between points A and B as a function of temperature. The voltage is composed of the voltage due to the carbon and copper elements and to the contact over-voltage. The decrease in voltage is due to the change of pressure as copper expands more than carbon.

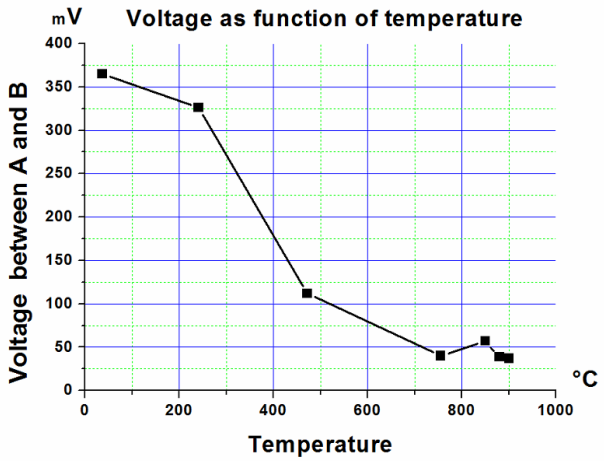

Figure 5: Voltage over the sample as a function of temperature

In order to separate the impact of temperature from the impact of pressure, measurements were performed at room temperature while varying the pressure in a hydrostatic press as shown in Figure 6.

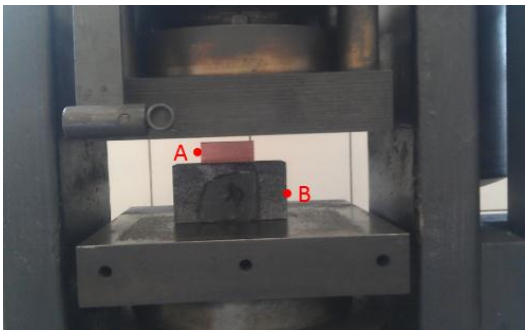

Figure 6: Contact voltage measurements as a function of pressure at room temperature

Figure 7 shows the voltage between point A and B (copper, carbon and contact resistance) as a function of pressure at room temperature. As the electrical contact resistance is very sensitive to the status of the surface, two type of surface treatments were considered for the test. Obviously increasing pressure decreases the electrical contact resistance. The surface "treatment" plays also an important role.

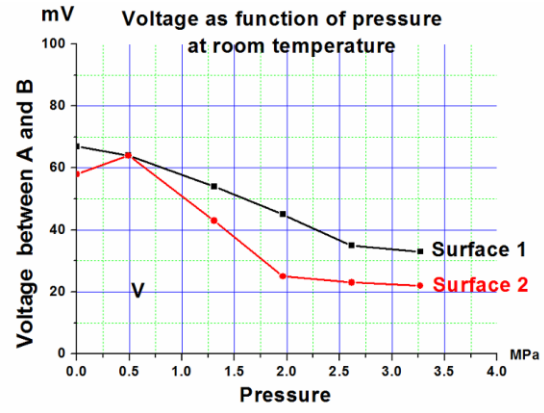

Figure 7: Voltage between A and B as a function of pressure for two type of copper surface treatment

By using these measurements and numerical simulation the electrical contact resistance between copper and carbon as function of temperature and pressure can be determined. The good news is that it corresponds to less than 30 mV in standard operation conditions (about 850°C, 3MPa, 1 A/cm2) if the surface conditions are realized.

Before going to an industrial test, numerical simulation was performed to determine the copper bars dimensions, the steel bar dimensions, the expected CVD, temperature and heat loss.

Numerical simulation

First a 3D slice model of a cell (Figure 8) including two collector bars and one anode was used. In a second stage, when the heat balance was satisfied, a full 3D cell model was used to determine the metal velocity field, metal deformation and cell magneto-hydrodynamic stability.

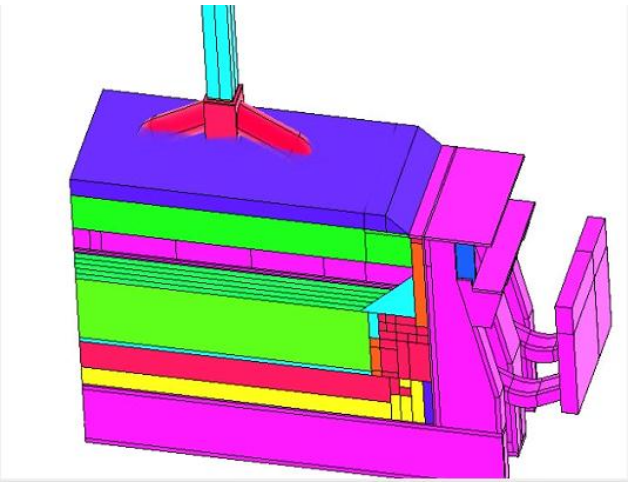

Figure 8: 3D-slice, two collector bars, one anode.

By using a 70 mm X 70 mm copper bar inside the cell connected to 45 cm of steel bar at the end very interesting results came out assuming 20 mV contact voltage drop.

The voltage from liquid metal to the aluminium flexes (end of the steel bar) was found to be 168 mV without any contact voltage. It is equal to 347 mV with the standard steel bars. Assuming 30 mV contact voltage between copper and carbon and zero contact between copper and steel this represents a potential saving of 149 mV. Figure 9 shows the calculated electrical potential. It is interesting to see that the equipotential line is horizontal. This means that the current is vertical in the liquid metal.

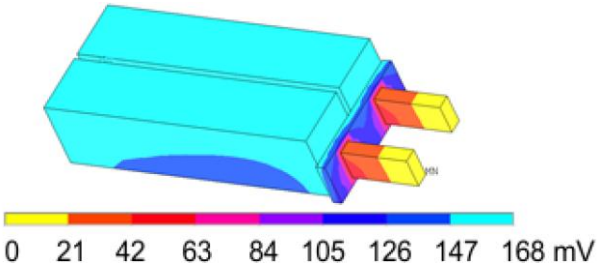

Figure 9: Calculated CVD liquid metal to collector bar (V) (no electrical contact resistance)

One fear was that the copper might reach its melting temperature which is 1085°C. In this respect the collector bar temperature was calculated assuming that the liquid metal in the cell is 965 °C and then 1100°C at steady state. Under such conditions the copper bars will never reach the melting point as the temperature gradient is typically 15 °C between the cathode surface and the collector bar. This value depends on the properties of the cathode block. Figure 10 shows the expected temperature under operation conditions when the liquid metal is 965°C. It can be observed that the steel part is necessary to decrease the temperature from 800 °C to 200°C at the end of the bar while the copper bar (thin part) varies from 950°C to 800°C from the center of the cell to the steel bar.

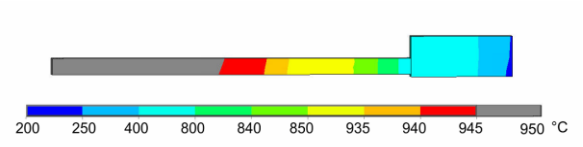

Figure 10: Temperature of the copper bar assuming 965°C liquid metal in the cell

Another important factor is the thermal expansion. Copper expands typically 3 to 4 times more than carbon. Therefore, thermo-mechanical stresses develop during the startup phase of the cell that could damage the cathode. Figure 11 shows how the cathode and copper bar expand when the temperature is changed from room temperature to the operating temperature. The length is increased by 24 mm towards the outside of the cathode and 5 mm towards the inside.

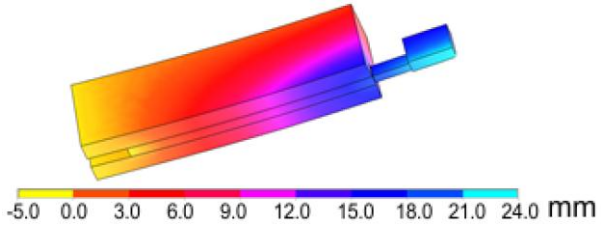

Figure 11: Cathode and copper bar thermal expansion from room temperature to operating temperature

Industrial test

Based on the laboratory and modeling results a test was realized in an industrial electrolysis cell. Figure 12 shows the copper bar connected to the steel end.

Figure 12: Copper bar coupled to a steel bar

It was decided to use a threaded connection to connect the copper bar to the steel bar, as shown in Figure 13.

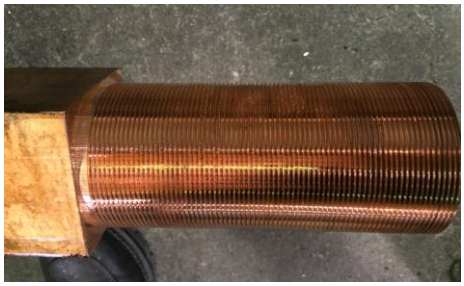

Figure 13: Copper thread

In order to avoid any risk of cracking the carbon cathode due to mechanical stresses generated by the thermal expansion of the copper bar, a gap filled with ramming paste was used between the copper bar and the carbon cathode. The copper bar was insulated electrically over some distance at the end of the block by an insulating cloth as shown in Figure 14.

Figure 14: Block, ramming paste and electrical insulation

The bars were equipped with electrical potential and temperature sensors at two locations as shown in Figure 15.

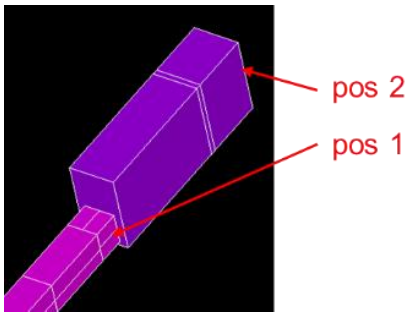

Figure 15: Voltage and temperature measurements

It was of high interest to record the temperature and the voltage at these locations as it would indicate any risk of high temperature

for the copper bar and tell us about the electrical contact resistance between the copper and the steel bar of the threaded connection. Both could be compared to the modeling results. In fact, very soon after the cell startup, a higher temperature was measured at position 1 on the copper bar. Figure 16 shows the copper temperature for two bars over a one month period including the startup period. The maximum temperature at the end of the copper bar during the startup phase was 900 °C. It reached stability after 10 days at 810 °C. When the temperature reached 900°C, the bath temperature in the cell was close to 1100°C. One thermocouple was lost after 9 days. Modeling predicted 800 °C which is in line with the measurements. However very soon the higher measured temperature was attributed to heat produced at the threaded contact Cu-Steel. This was confirmed by voltage measurements from the end of the copper bar at position 1 to the end of the steel bar at position 2.

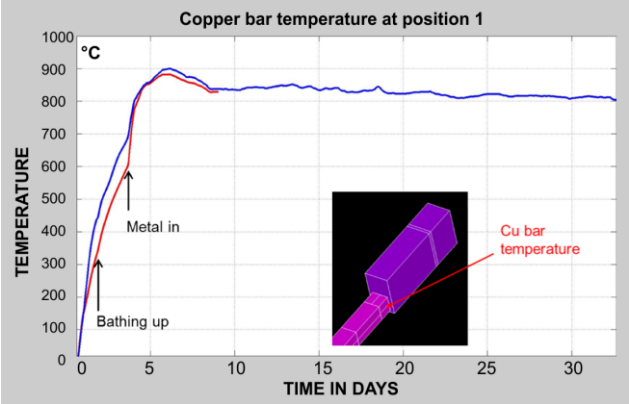

Figure 16: Temperature at the end of the copper bar during the first 30 days

The electrical potential was recorded every second and is shown for the first 147 days in Figure 17. A drastic increase of the voltage can be observed for the two measured bars after 40 days. The initial voltage was already higher than calculated from the numerical model.

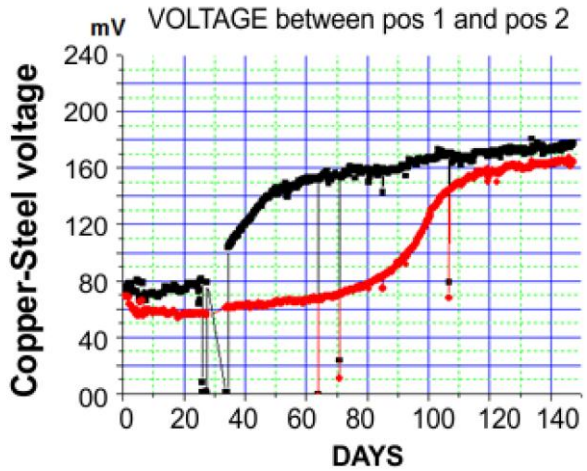

Figure 17: Voltage drop from position 1 to 2 for two coll. bars

The targeted electrical resistance from the end of the copper bar to the end of the steel bar was 10 μΩ. Figure 18 shows the evolution of the electrical resistance which started around 40 μΩ and reached up to 220 μΩ for one bar after 147 days. It confirms that the threaded connection cannot be used or was not realized as it should. In other words the threaded connection did not work as expected, most likely due to copper oxidation or other type of corrosion at the copper surface inside the steel bar! This affects the CVD and is not acceptable. As a consequence, a new type of connection was designed.

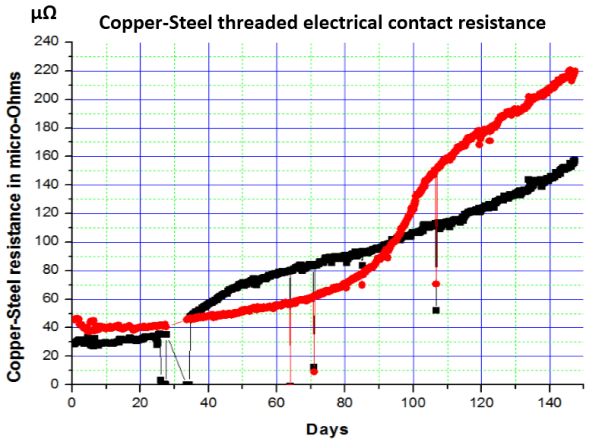

Figure 18: Cu-Steel electrical resistance

A second parameter affected the CVD. Indeed, the use of ramming paste is not optimal for the electrical contact between the copper and the cathode. Soon after startup, the CVD measurements led to an average electrical resistance of 120 μΩ. This is much higher than the numerical model results of 28 μΩ. In fact it is twice more resistive than the existing conventional steel bar showing 60 μΩ. Obviously this design is not recommended. However the experiment showed that copper can be considered as a candidate for extracting the current from the cathode.

Next steps

Based on these results, a new cathode design was realized using two copper bars directly imbedded in the cathode and connected to a steel bar as shown in Figure 19.

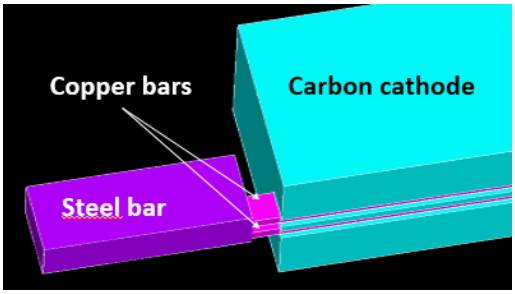

Figure 19: Copper bars imbedded in carbon cathode

Using appropriate dimensions and contacts, this solution predicts a CVD of 190 mV which is more than 150 mV lower than the solution using steel bars. At the same time modeling predicts that the current density at the cathode surface is very smooth ranging from 0.7 A/cm^2 to maximum 1 A/cm^2 as shown in Figure 20.

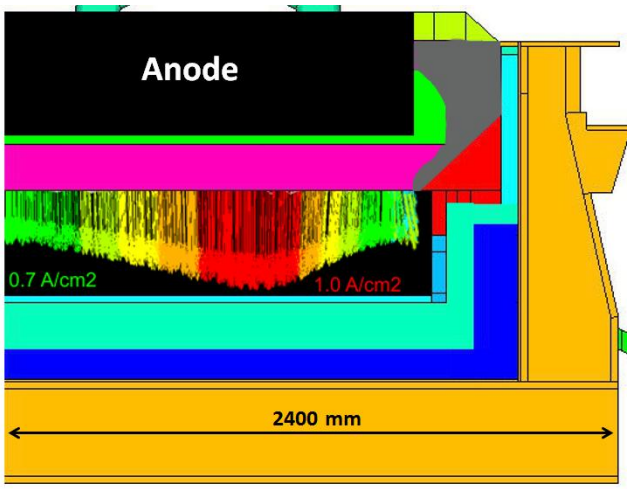

Figure 20: Current density at cathode surface

Another benefit of using copper bars is the impact on the magneto-hydrodynamic cell stability. Figure 21 shows the current density inside the liquid metal. There is quasi no horizontal current flowing towards the cathode edge. In other words the current is almost vertical and this helps at decreasing the ACD while keeping a stable cell.

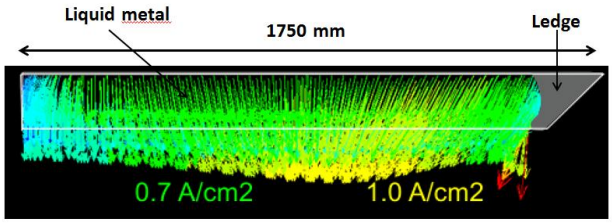

Figure 21: Current density inside the liquid metal

Therefore a new industrial test needs to be performed using this new cathode design.

Conclusions

A new concept has been patented and is presently implemented in a cell. The first industrial test failed due to the poor electrical contact of the threaded connection between copper and steel. The use of ramming paste as interface between the copper and the cathode was most likely also a weakness. The positive result is that after 150 days the copper is still conducting current and the decrease of intensity is related to the threaded connection. Laboratory tests permitted to identify important parameters such as the pressure between copper and the carbon cathode. Modeling work confirmed possibilities of using copper bars inside the cathode leading to very low CVD and improved MHD.

The measurements showed that:

- The contact voltage between copper and carbon must be lower than 30 mV at 850°C with 1 A/cm2 and about 3MPa pressure
- A threaded connection betweem copper and steel is most likely not a solution
- Ramming paste interface between the copper bar and the carbon cathode is not very favorable
- Copper is not affected in the cathode even when the temperature is reacing 1100 °C in the liquid metal

As comment let us mention that there are numerous potential advantages when using copper bars:

- No need to preheat the cathode
- No need of cast iron
- Very easy to recycle 95% of the copper
- Very low CVD
- Improved cell MHD stability

This must lead to:

- Lower cell specific energy consumption
- Longer cell life (less electro-erosion)
- Deeper cell cavity (low collector bars)
- Lighter cathode (cheaper)

Acknowledgments

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