# AL24 - Experience with Homogeneous Cu Collector Bars Directly Fitted into Cathode Blocks

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**Abstract**

Cu is increasingly being introduced into collector bar solutions to facilitate amperage increase and energy savings. The most common solution is to fit a copper insert into existing steel collector bars, but this is associated with extra cost as well as challenging recycling at the end of life. Since 2013, Hydro Aluminium has tested a solution where homogeneous Cu bars (cylinders) are fitted directly into the cathode blocks without any cast iron or rodding solution. The solution is very cost efficient with a high potential for recycling of Cu at the end of life. The initial results showed a significantly lower cathode resistance, but a higher increase in cathode resistance with time than for normal steel collector bars. The autopsy results of a preliminary stopped cell showed severe reaction and swelling of the Cu cylinders and a corresponding delamination of the cathode blocks. The degradation of the Cu cylinders and cathode block assembly continued steadily until 1700-2350 days of operation where a dramatic increase of cathode resistance occurred. The rapid increase in cathode resistance led to a rapid increase in temperature followed by melting of the Cu collector cylinders and a dramatic tap-out. The failure mechanisms are discussed.

**Keywords:** Aluminium electrolysis cells, Copper collector bars, Cathode resistance.

## 1. Introduction

Cu-inserts in collector bars have more and more replaced the homogeneous steel bars in Hall-Hérault electrolysis cells [1–3]. Cu is an excellent electrical conductor, and the utilization of Cu enables lower cathode voltage drops without increasing the size of the collector bar. Even though Cu is similar in cost to steel when comparing cost/mV of cathode voltage drop (CVD), the Cu-insert assembly imposes a higher cost. In addition, recycling of the Cu at end of life is challenging and a sealing method to fix the collector bar into the cathode block is still needed.

A low-cost solution using homogeneous Cu cylinders directly fitted into a hole in the cathode blocks is described here. The potential benefits of this solution are:

- Low cost (~LME Cu),
- Low CVD combined with high useful amount of carbon in the cathode block,
- Easy and low-cost installation,
- No cast iron rodding,
- Easy to recycle at end of life.

## 2. Direct Connection

As part of this concept, direct contact between the collector bar cylinder and the cathode block by thermal fitting was utilized. The thermal expansion of Cu, steel and cathode blocks is shown in Figure 1. Steel has a disadvantageous phase transition (with shrinkage) at the operating temperature range which limits its use in direct connection with carbon. Cu has a continuous positive thermal expansion that is higher than the graphitized cathode block and is in addition quite soft at the operating temperature. This makes homogeneous Cu collector bar cylinders a potential candidate for direct thermal fitting.

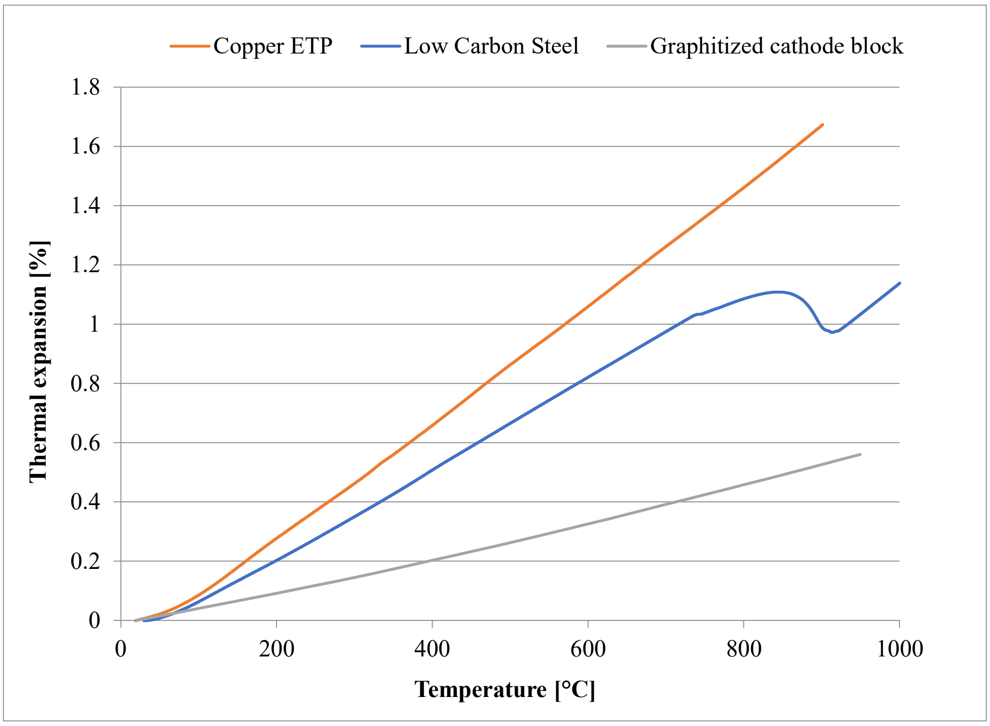


**Figure 1. Thermal expansion of low carbon steel, Cu and a typical graphitized cathode block.**

A disadvantage of thermal fitting is that a high contact pressure is desired but not so high that the block cracks. This can be achieved with high dimensional precision, but machining to low tolerances is costly. An intermediate solution was chosen where some dimensional deviations in width and straightness could be tolerated.

To check for crack formation during preheating, dummy tests were carried out in a furnace. Pieces of typical cathode blocks were machined according to standard tolerances with holes and Ø 60 mm Cu cylinders, electrolytic tough pitch (ETP) grade, as shown in Figure 2. The assembly was heated to 1000 °C, and the block was visually inspected for cracks after the test. No cracks were observed. To provoke cracks, one Cu cylinder was machined to be slightly larger than the hole in the cathode block sample. The Cu cylinder was then cooled in liquid nitrogen (−195.8 °C) and fitted into the hole. The assembly was heated to 1000 °C and the result is shown in Figure 3. Minor cracks occurred, but crack formation due to thermal expansion was not considered a showstopper for the concept.

**Figure 2. Initial crack testing. Left: before testing. Right: after testing, no visible cracks.**

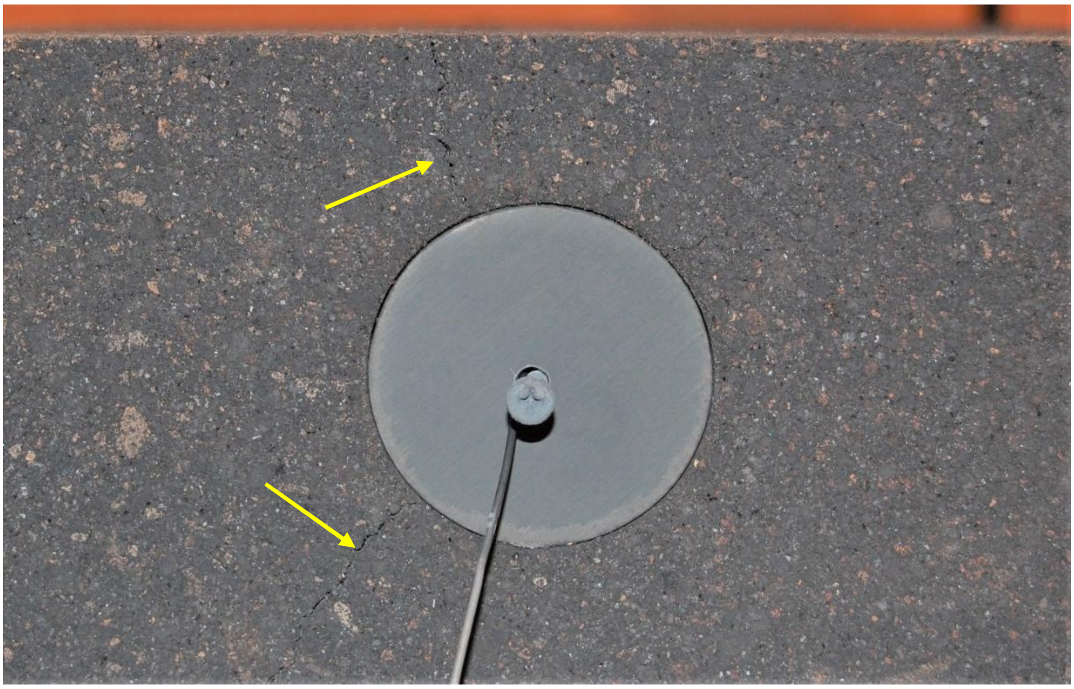

**Figure 3. Assembly after crack testing with large Cu cylinder cooled in liquid nitrogen before insertion into cathode block sample. Arrows point at visible cracks.**

## 3. Testing with One Block in a Cell

As several items with the concept were new, the risk was considered to be high. Therefore, the first full scale trial was with one block in a normal operating cell. The cell was preheated with gas, and the current distribution development is shown in Figure 4. The block with homogeneous Cu cylinders pulled more current than the standard blocks, and this situation lasted until the last year of operation.

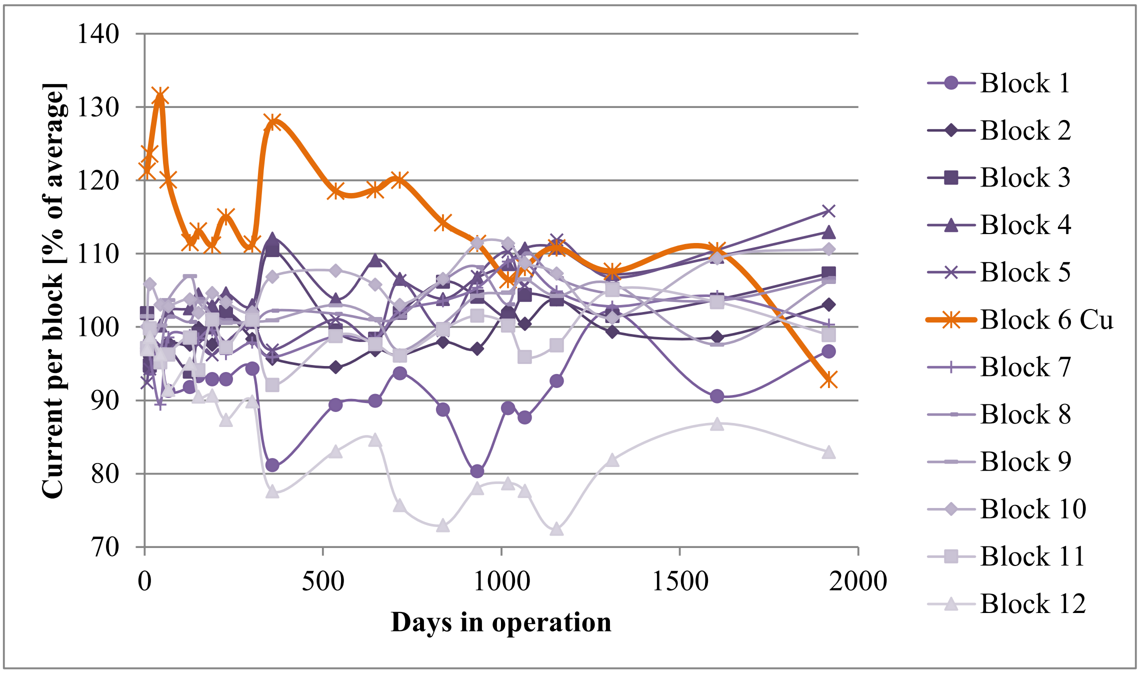


**Figure 4. Current pull in the one block test (in a cell with 12 blocks).**

The concept was also tested in cells started with electrical preheating. A challenge with thermal fitting is that the contact resistance is high in the cold state. A test with one block of homogeneous Cu cylinders in a standard cell during electrical preheating is shown in Figure 5. The current pick-up is slower than the standard collector bars but ends also up higher than the standard collector bars during start-up. Later, complete cells with homogeneous Cu cylinders were successfully started with electrical preheating.

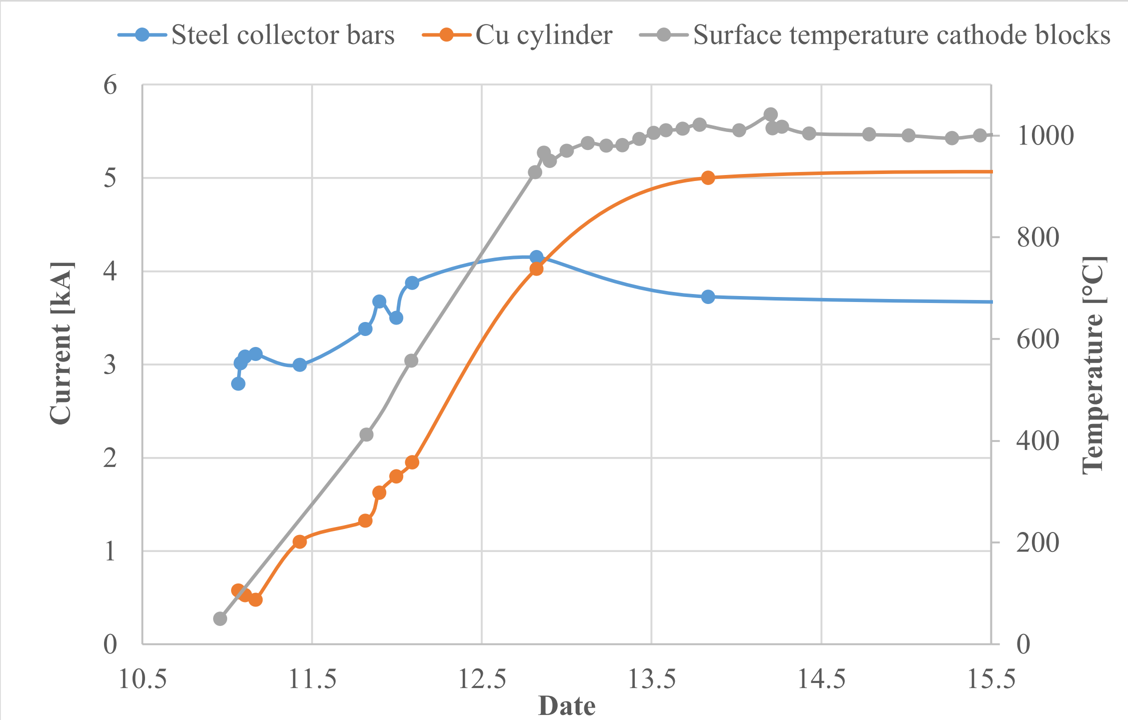


**Figure 5. Current pull during electrical preheating of a cell with one Cu cylinder block compared with adjacent blocks with standard steel collector bars.**

## 4. Full Cell Test

The next step in the test program was to start a cell fully equipped with homogeneous Cu cylinders. After a successful start-up, the cathodic current distribution was measured regularly. The development of current distribution with time is shown in Figure 6a. The data shows a very even current distribution with a low standard deviation (6-10 %), except for the last measurement after 1392 days.

Furthermore, five additional similar cells were started fully equipped with Cu-cylinders. The development of cathode voltage drop (CVD) compared with reference cells with standard steel collector bars and the same cathode block type is shown in Figure 6b. The Cu cylinder cells started lower in CVD than the standard steel bars, as modeled. However, the CVD of the Cu cylinder cells increased more rapidly than the standard cells, and after approximately three years of operation the CVD was similar. The average CVD during the pot life was also similar.

Other operational parameters for the Cu cylinder cells are shown in Table 1, averaged over the entire pot life. Interestingly, the current efficiency is 0.8 % higher than the reference cells. In addition, the cell-to-cell voltage is lower and a reduction of 0.2 kWh/kg Al in specific energy consumption is observed. A longer pot life for cells with Cu-cylinders is partly due to more cathode block carbon available for erosion.

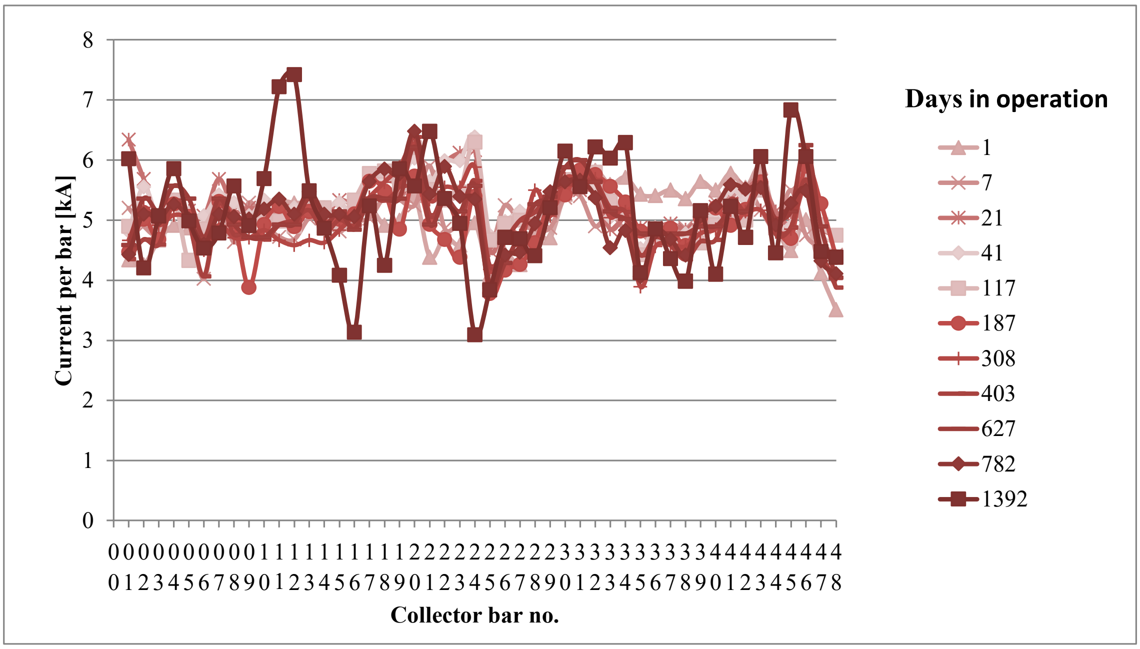


**Figure 6a. Cathodic current distribution development for Cu cylinder test cell.**

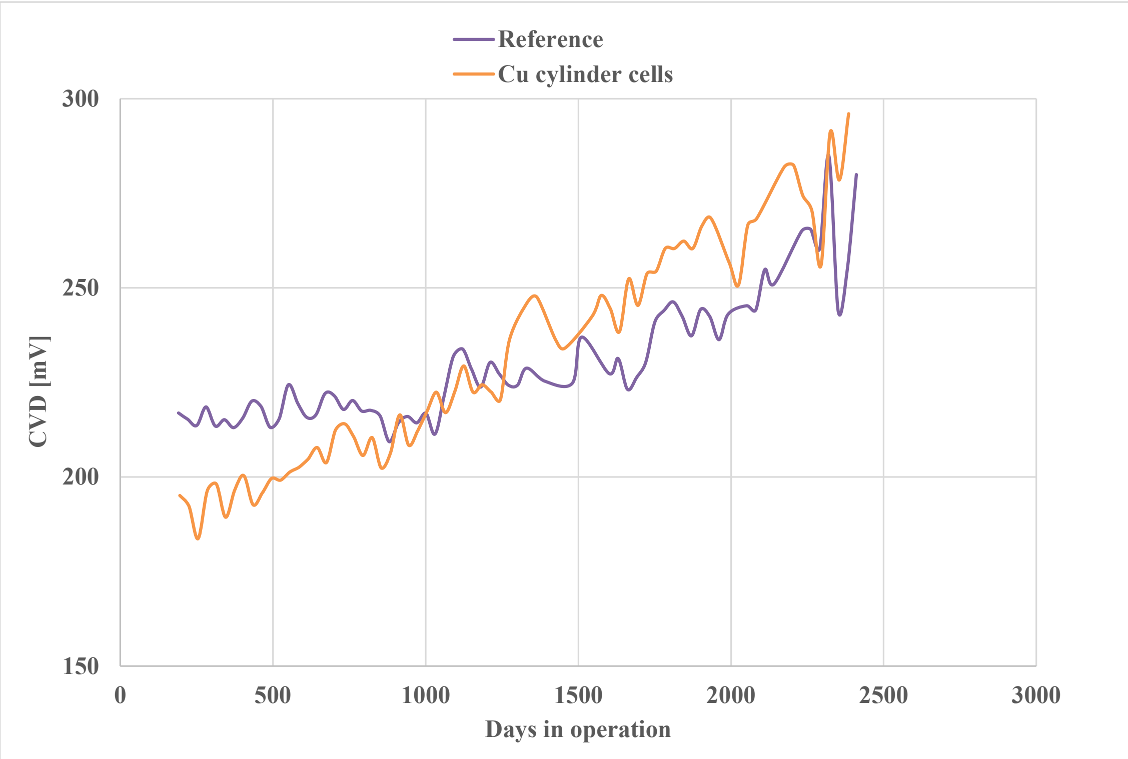


**Figure 6b. CVD development for Cu cylinders cells compared with reference cells with standard steel collector bars and the same cathode block type.**

**Table 1. Average operational parameters for Cu cylinder cells vs. reference cells over pot life.**

| Parameter | Cu cylinder vs. Reference cells |
|---|---|
| Current efficiency [%] | +0.8 |
| Na in metal [ppm] | +1.9 |
| Energy consumption [kWh/kg Al] | -0.2 |
| Noise [μΩ] | +0.01 |
| Cathode voltage drop [mV] | -2.2 |
| Cell to cell voltage [V] | -0.024 |
| Anode effect frequency | +0.04 |
| Pot life [days] | +307 |

## 5. Autopsy Observations

The first fully equipped Cu cylinder cell was deliberately stopped after approximately 1400 days of operation. A typical cross-section of the cathode blocks with Cu cylinders is shown in Figure 7, and a cross-section cut of a typical Cu cylinder in Figure 8. A mostly horizontal crack is formed at the level of the middle of the holes. The Cu cylinder has grown in height and a metallic phase is seen horizontally in the crack, extending from the original Cu cylinder. The horizontal cracks are 10-12 mm at the thickest around the Cu cylinders, and the crack is extending to the block side/bottom surface. Furthermore, two phases were visually observed in the reacted Cu cylinders, as shown in Figure 7 and 8; one phase is of brass color, and one is of silvery color. The chemical composition of the brass-colored phase investigated by SEM/EDS to be 87 wt% Cu/12 wt% Al, and the silvery colored phase was 63 wt% Cu/36 wt% Al.

**Figure 7. Typical cross-section of a typical cathode block with reacted Cu-cylinder.**

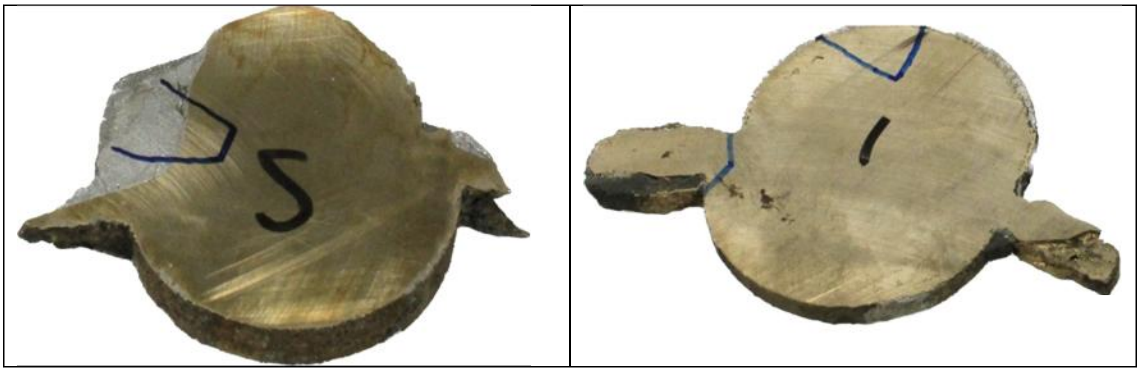


**Figure 8. Cross-section reacted Cu-cylinders after approx. 1400 days in operation. Left: cylinder with mostly brass colored phase with silvery phase in upper left area. Right: homogeneous brass colored cylinder.**

One other cell in a different potline was stopped deliberately after 1100 days in operation. A cross-section cut of typical Cu cylinder from this cell is shown in Figure 9. Here the reaction had proceeded less than in the first cell shown in Figure 8, and there is still some virgin Cu-phase left in the used Cu cylinder. Nevertheless, the cathode block had also cracked here, similarly as shown in Figure 7.

**Figure 9. Cross-section reacted Cu-cylinders after approx. 1100 days in operation.**

## 6. Discussion

There are several serious degradations observed in cells with Cu cylinders:

- Horizonal cracking/delamination of the blocks at the Cu cylinder level in the block,
- Reaction between the Cu cylinder and Al causing volume expansion,
- Reaction between the Cu cylinder and Al forming a liquid alloy,
- Increased resistivity of the Cu cylinder due to intermetallic formation.

The first observation is believed to be a consequence of the second observation.

In cell designs using steel collector bars with cast iron in contact with the cathode block, reactions occur to a small degree at the surface of the collector bar/cathode block interface [4]. Al is often leaking in joints and might wet the surface of the collector bar/cast iron and thus reacting at the interface. It is also possible that intermetallic phases form due to the reaction between bath, Na intercalated in the cathode block and the steel/cast iron [4]. However, this reaction is limited and usually does not create cracks in the cathode blocks.

The same mechanism is probably more critical for the Cu-cylinders than for steel bars. Assuming that the block does not crack initially, there is no path for liquid Al to reach the Cu cylinder. The only source of Al in contact with the cylinders is the bath penetration in the cathode block porosity. The Na formed at the cathode, intercalate in the cathode block and the following reaction can occur:

$$Na(intercalated) + AlF_3 + Cu \dashrightarrow CuAl_x + NaF \quad (1)$$

A thermodynamic calculation of the system Cu-$Na_3AlF_6$-Na is shown in Figure 10. The graph shows the amount of Al in the Cu-Al alloy as function of Na(g) activity. The Na activity in the cathode block is estimated to be 0.02-0.03 by Solheim [5], which limits the Al content in the alloy in the reaction to approximately 12 wt% Al. A 10 % Al alloy corresponds to the brass-colored phase, but this does not explain the formation of a silvery phase with approximately 36 % Al. Formation of Cu-Al alloys with 15 wt% Al or more requires much higher Na activity than what is given in literature [5], or that the Al source is liquid Al with close to unit activity. There were several observations of Al metal in the transversal joints, and the reaction between the Cu cylinder and liquid Al might have occurred after the block cracked.

The volume expansion when Al is added to Cu is shown in Figure 11. A 10 % addition of Al to the Cu results in a volume increase of approximately 30 %, which is sufficient to crack the blocks. The Cu-rich intermetallic phases are solid, and any volume growth of the cylinder will apply pressure on the block.

The Al-Cu phase diagram is shown in Figure 12, and the composition of the two phases analyzed are marked in the figure. The silvery phase has a composition that is liquid at 800 °C or higher, which means that some part of the Cu cylinder was molten at the operating temperature. This observation was also supported by the presence of empty space in some of the holes.

Another important parameter is the resistivity increase of the Cu-Al alloy compared to the pure Cu cylinder. The resistivity of the brass-colored alloy (approximately 10 wt% Al) was measured to be approximately three times higher than for the virgin Cu at 900 °C. This increase in resistance will also contribute to the increase in CVD as the reaction takes place. The cracking, or delamination of the cathode blocks, will also cause increased CVD. The contact pressure will drop when the blocks crack as well as the contact area around the hole in the block is reduced. The reduced contact area is however increased by the growth of Cu-Al alloy in the crack area.

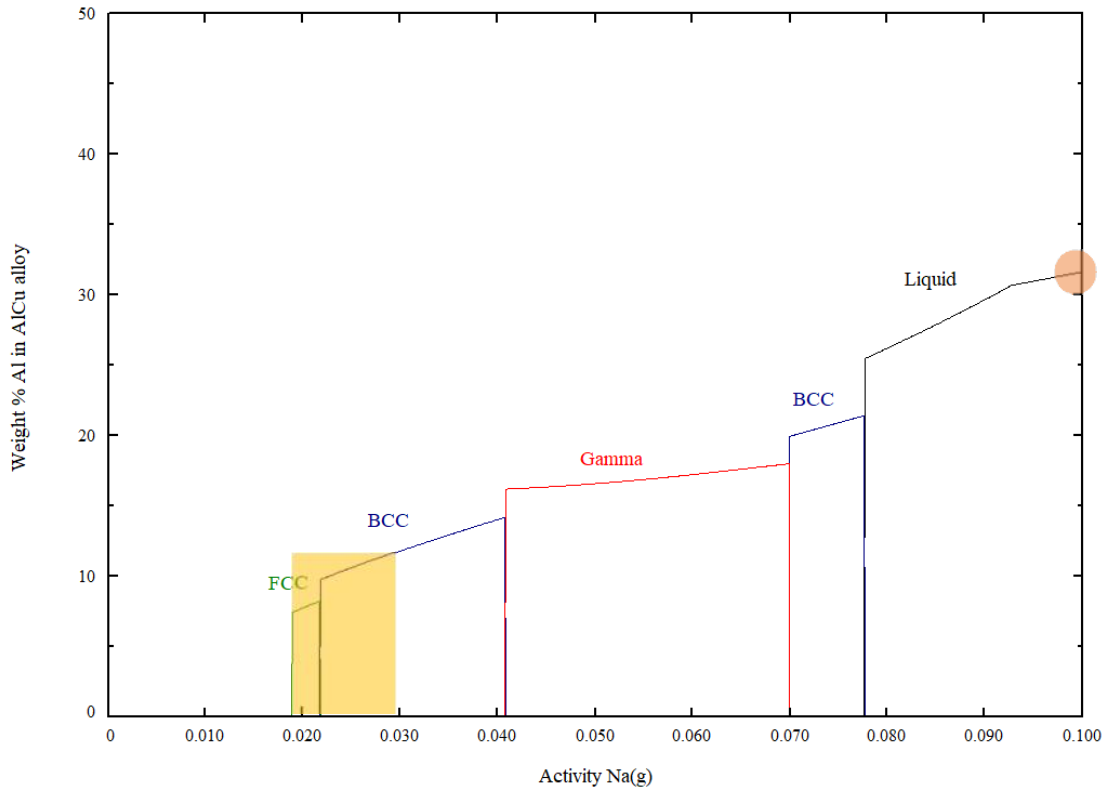


**Figure 10. Thermodynamic calculation (Factsage 8.2) of the amount of Al in the Cu-Al alloy in contact with bath, as function of Na(g) activity at 900 °C. Yellow area shows typical Na pressure in the cathode according to [5], which also corresponds to the bronze colored phase formed in the cylinders. The red circle shows the composition of the silvery phase observed in the cylinders.**

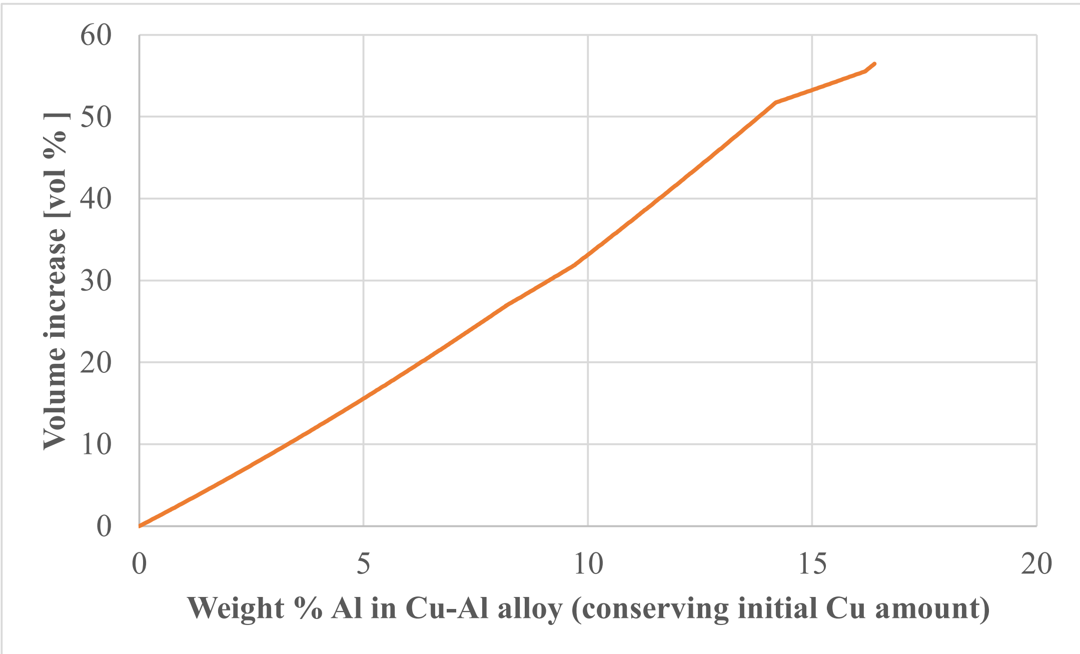


**Figure 11: Volume increase when Al is added to Cu at 900 °C. Data from Factsage 8.2 calculation.**

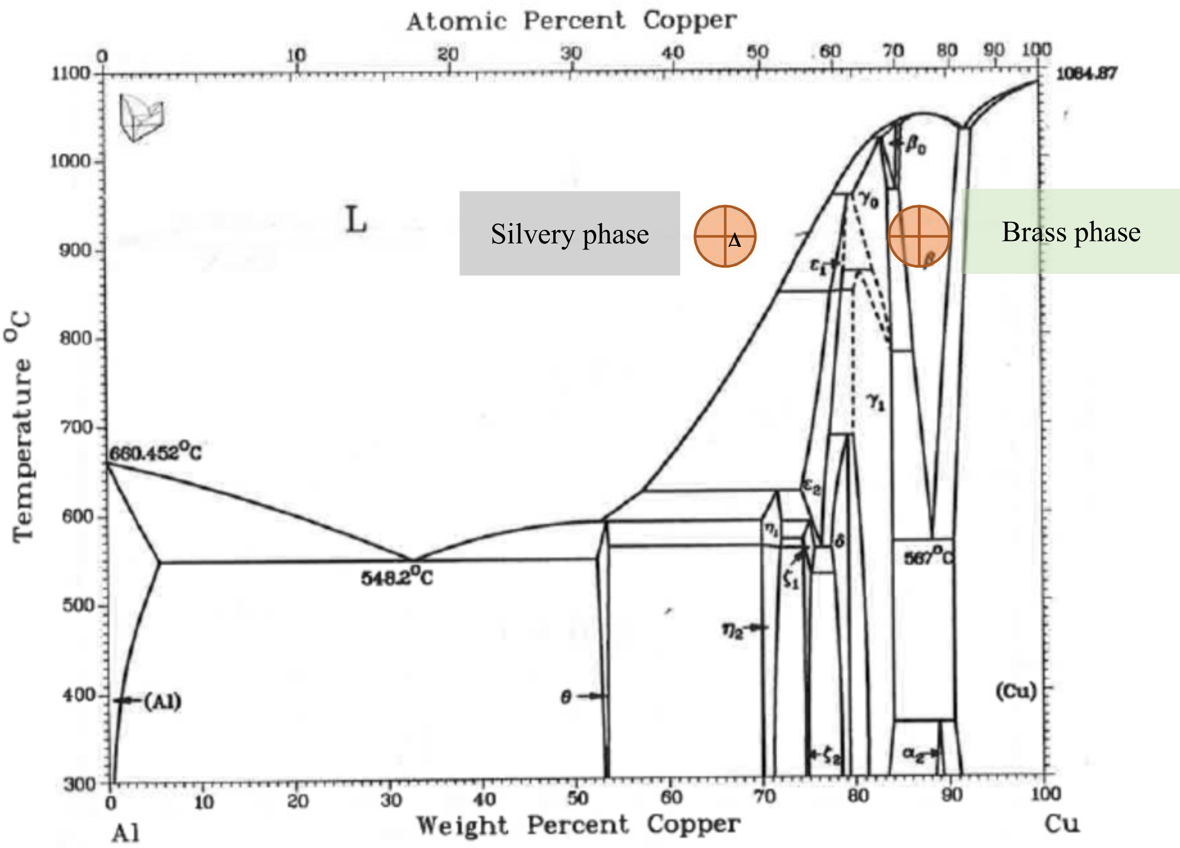


**Figure 12 The Al-Cu phase diagram [6].**

## 7. End of Life Behavior

Even though the cells had extensive laminar cracking of the cathode blocks and degradation of the Cu cylinders, the cells continued to operate well until reaching expected pot life. However, several of the Cu cylinder cells experienced a sudden increase in cell voltage resulting in a high temperature and a dramatic tap-out where bath and metal burst out of the cell in several locations. The noise level and cell voltage are shown in Figure 13. A few hours before tap-out the noise increases, the cell voltage increases dramatically and causes melting of the Cu cylinders and a cascade effect of increased resistance. The melting of the Cu cylinders and the high bath temperature led to several open paths for metal and bath to exit the cell. One example is shown in Figure 14.

The dramatic events at the end of life appeared with little or no warning, thus exposing a very high risk for the pot line operation. The remaining Cu cylinder cells were stopped in a controlled manner.

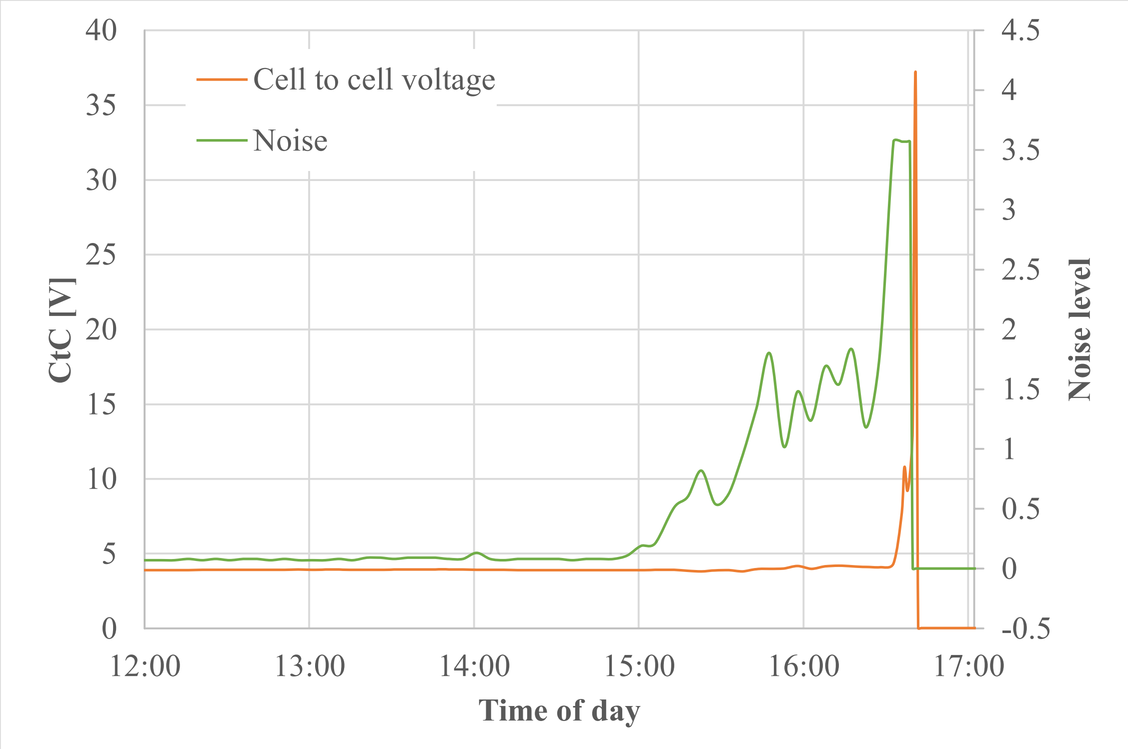


**Figure 13. Noise and cell to cell voltage before tap-out after 2350 days in operation. CTC [V] = Cell-to-cell voltage.**


**Figure 14. Example of tap-out area.**

## 8. Conclusions

A concept where homogeneous Cu cylinders are fitted directly into the cathode blocks without any cast iron or rodding solution has been tested from lab scale to full operation. The solution is cost efficient with a high potential for recycling of Cu at the end of life. The initial results showed a significantly lower cathode resistance, but a higher increase in cathode resistance with time than for normal steel collector bars. The autopsy results of a preliminary stopped cell showed severe reaction and swelling of the Cu cylinders and a corresponding delamination of the cathode blocks. The degradation of the Cu collector cylinders and cathode block assembly continued steadily until 1700-2350 days of operation until a dramatic increase of cathode resistance occurred. The rapid increase in cathode resistance led to a rapid increase in temperature followed by melting of the Cu cylinders and a dramatic tap-out. The remaining Cu cylinders cells were stopped in a controlled manner.

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