

Industrial Trials of Super Conductive Cathode Collector Bar Pastes in 300 kA Cells in Yunnan Aluminium Smelter

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Abstract

Industrial application trials of super conductive bar pastes (super pastes) have been conducted in two aluminum smelters in China. There are presently three groups 300 kA trial cells with type 2 super pastes (two cells per group) in Yunnan Aluminium smelter. These six trial cells were started in March, July, and December of 2024, respectively. The installation procedure of the super pastes is the same as that of traditional cold bar pastes, i.e.: rammed at room temperature. The first group of two trial cells have been in operation for over one year now. Compared with two reference cells using Elkem high conductive bar paste (high paste), the cathode voltage drops (CVDs) of these two trial cells are on average 19.8 mV lower than that of the two reference cells. The CVD developments of the test and reference cells can be well modelled with the Electric Excel Cathode Model by adjusting the contact electrical resistivities. The results show that the contact resistivities increased to four to over six times of the original value within 15 months operation. Reducing the width ratio of the cathode bar slot to the steel bar can increase the pressure on the bar paste, thereby reducing the interface contact resistance and hence the CVD, but the effect seems to last a few months only and the CVD becomes similar to that of the cells without reducing the width ratio. Since reducing the width ratio will increase the risk of cracking the cathode block by the steel bar expansion, it must be very carefully done. The impact of type 2 super pastes on current efficiency and DC power consumption is small, and both indicators have minor improvements or are roughly equivalent. The super paste has not yet been finalized and is still under continuous improvement. More industrial trials of super pastes are currently underway or planned, and the trial results will be publicly reported in the future.

Keywords: Super paste, Industrial trial, Aluminium cell, Cathode rodding.

1. Introduction

At present, the rodding methods of cathode carbon blocks and cathode steel bars (usually low-carbon steel) in aluminum electrolysis cells are divided into two methods: cathode bar paste ramming and cast-iron rodding. The main advantages of cast iron rodding are that cast iron has a low resistivity ($< 1 \mu\Omega\cdot\text{m}$ at room temperature) and low contact resistivity with the steel bar (0 at high temperatures, but there is a quite high contact resistivity with the cathode block instead).

However, cast iron rodding requires a high-temperature process of about 1 400 °C, which has a large thermal shock and is prone to cracking of carbon blocks. The scrap rate is high, and the cost and health, safety and environmental risks are also high. When using the cathode paste bonding method, high conductive bar paste (hereinafter referred to as high paste) with graphite and electrically calcined anthracite (ECA) as aggregates is currently mainly used. Its electrical resistivity is usually between 25 and 40 $\mu\Omega\cdot\text{m}$ at room temperature. Its contact resistivity with steel bars is also high. The main advantages of the cathode paste ramming method are room temperature installation, no thermal shock, and no health, safety or environmental risks.

In order to combine the advantages of cathode paste consolidation and cast-iron rodding and overcome the above-mentioned disadvantages, Elkem Carbon (China) Co., Ltd. (hereinafter referred to as Elkem) successfully developed two types of super conductive bar pastes (hereinafter referred to as Type 1 super pastes and Type 2 super pastes) in 2023. The type 2 super pastes presently have 3 products, namely SCP2-1, SCP2-2 and SCP2-3. The typical room temperature properties of Type 2 super pastes and Elkem high paste BC20 are listed in Table 1.

Table 1. Typical room temperature properties of three different bar pastes.

Paste	SCP2-2	SCP2-3	High paste BC20
Baked electrical resistivity ($\mu\Omega\cdot\text{m}$)	1.5	3.0	32
Baked apparent density (g/cm^3)	3.8	3.3	1.48
Baked compressive strength (MPa)	35	22	23
Unbaked electrical resistivity ($\mu\Omega\cdot\text{m}$)	> 1 200	600	500

Many aluminium smelters pay great attention to the rodding voltage drop which is directly linked to the unbaked electrical resistivity of a bar paste, that is why we developed super paste SCP2-3 which has the lowest unbaked resistivity among the super pastes.

2. Electrical Resistivity at High Temperature

The electrical resistivity of the baked graphitic bar paste or high paste BC20 and type 2 super paste SCP2 were measured from room temperature to 950 °C. The unbaked samples were prepared at 20 °C according to ISO 14427 and then baked to 1 000 °C according to YS/T63.1. The High Temperature Resistivity Measurement System from Suzhou Micro-Structure Instrument (HTR-1) was used. The system was programmed to record data every 2 seconds. When two neighboring data were the same to the fourth decimal place, the system would not record the second one. The sample chamber is under vacuum with residue air pressure about 3 Pa. The cooling process from 950 °C to 850 °C or to 800 °C was controlled at 1.5 °C /min.

The electrical resistivity at high temperature of the high paste was first measured. The unbaked and baked densities of the high paste sample were 1.66 g/cm^3 and 1.49 g/cm^3 respectively. Figure 1 shows the resistivity as a function of temperature of BC20. It can be seen from Figure 1 that the initial room temperature electrical resistivity of the high paste is about 30.5 $\mu\Omega\cdot\text{m}$, it decreases almost all the way with temperature to the highest temperature, the minimum is 23.5 $\mu\Omega\cdot\text{m}$ at 946.3 °C. The cooling rate from 950 °C to 850 °C was controlled at 1.5 °C /min., and the resistivity increases almost all the way to the final temperature 31 °C, and the final resistivity is 30.38 $\mu\Omega\cdot\text{m}$ which is very close to the initial resistivity of 30.46 $\mu\Omega\cdot\text{m}$ at 20 °C. The resistivities in cooling and in heating almost coincided.

Measurement of the resistivity at high temperature of BC20 was conducted twice and the result shown here is from the second measurement. The main difference between the first measurement

and the second measurement is that the cooling from the top temperature of the first measurement was not controlled but just shut down the furnace and let it cool naturally. In addition, the residue air pressure of the first measurement was more than 10 Pa. The coincidence of the heating curve and the cooling curve was poor.

Figure 2 shows the electrical resistivity of super paste SCP2-2 as function of temperature. The unbaked and baked densities of the super paste were 4.03 g/cm³ and 3.69 g/cm³ respectively. The heating rate and the recording frequency are the same as those in the Figure 1. The cooling rate is slightly different from that in Figure 1, i.e.: from 950 °C to 800 °C instead of from 950 °C to 850 °C is controlled at 1.5 °C /min.

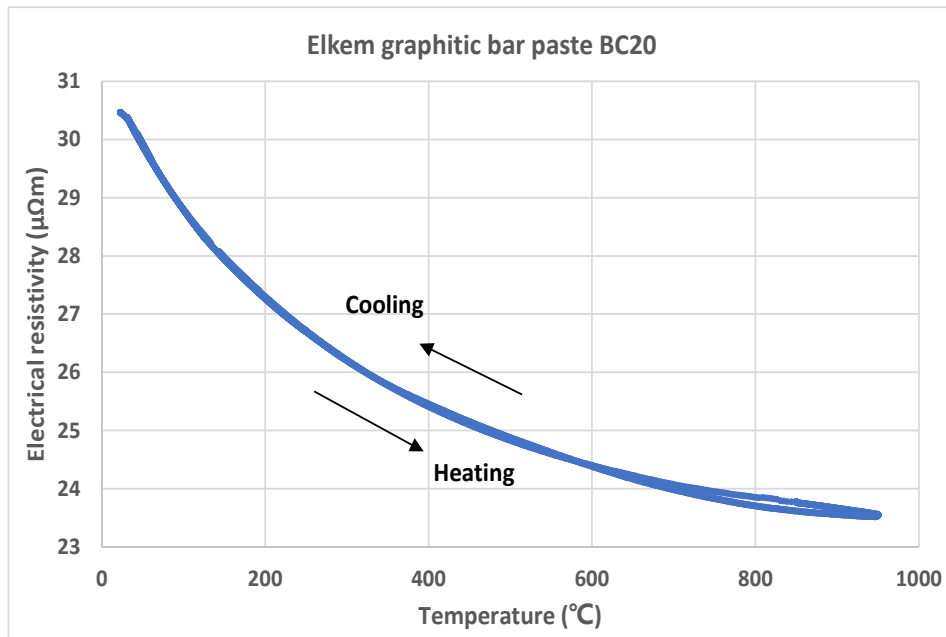


Figure 1. Electrical resistivity of graphitic bar paste as a function of temperature.

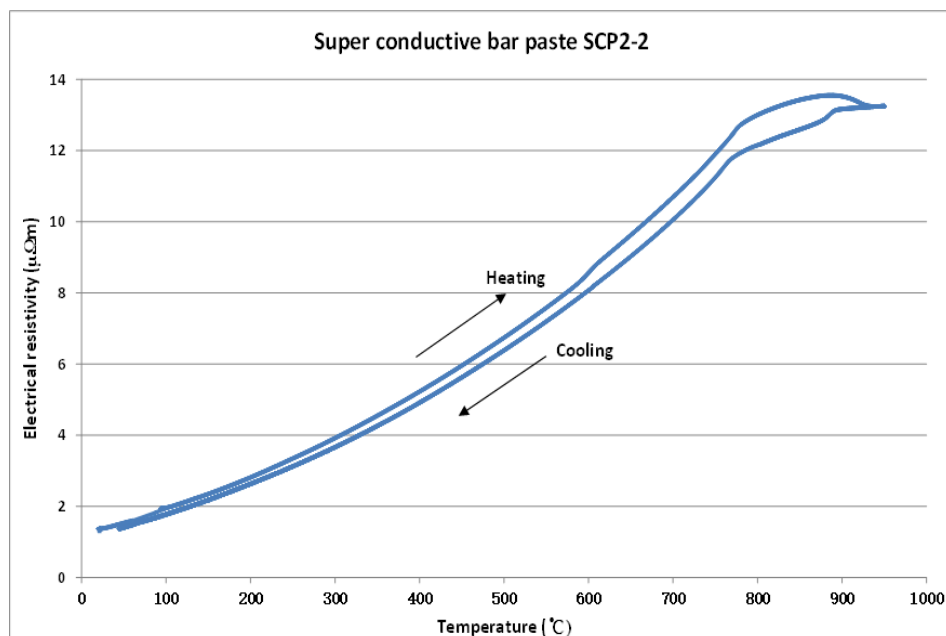


Figure 2. Electrical resistivity of super conductive bar paste Type 2 as a function of temperature.

It can be seen from Figure 2 that the electrical resistivity of super paste SCP2-2 increases with temperature all the time until close to 900 °C, and the maximum resistivity is 13.5 $\mu\Omega\cdot\text{m}$, then the resistivity fluctuates in the vicinity of the maximum. The resistivity starts to decrease when the temperature starts to decrease, and the resistivity in cooling is slightly less than that in heating. The reason is probably that the small sample got sintering for the 2nd time in heating and the resistivity was reduced. Extending the baking time from 2 hours to 6 hours can significantly reduce the resistivity difference in heating and cooling.

Please note that SCP2-2 consists of a group of recipes and the resistivity at room temperature varies from slightly less than 1 $\mu\Omega\cdot\text{m}$ to close to 2 $\mu\Omega\cdot\text{m}$. Measurement of the resistivity at high temperature was conducted only once for each recipe. More repetitions will be conducted to validate the conclusions.

3. Industrial Trial

3.1 The 300 kA Potline

The 300 kA potline was engineered by GAMI and started in 2004. There are 248 prebake cells and the capacity is 200 000 tonnes per year. The potline has been operating at 304 kA for a few years now. The cathode block quality had been 30 % graphitic for the first more than ten years and changed gradually to fully graphitic blocks from 2023, and it is now changing gradually to graphitized blocks. All test and reference cells in the present paper use 100 % graphitic cathode blocks and the typical properties are listed in Table 2; the properties of the graphitized blocks are included as comparison.

Table 2. Typical room temperature properties of graphitic blocks and graphitized blocks used by Yunnan Aluminium Smelter.

Cathode block	Apparent density (g/cm ³)	Electrical resistivity ($\mu\Omega\cdot\text{m}$)	Compressive strength (MPa)
100 % graphitic	1.63	18.5	30
Graphitized	1.65	10.5	24

The cathode block dimensions are length 3480 mm × width 510 mm × height 490 mm. The cathode block is double slotted, and the bar slot is 95 mm wide for the first two test cells and first two reference cells, and 90 mm wide for the rest of test and reference cells. The steel bar is 70 mm wide for all test and reference cells. The width ratio of the slot to the bar is 1.357 for the test and reference cells of the first group, and 1.286 for the 2nd and the 3rd groups of test and reference cells.

3.2 Rodding, Preheating and Starting

The rodding procedure is similar to that of a typical cold ramming paste and the cathode block, i.e., place four steel bars into the double slotted cathode block (two bars in one slot and the gap between two bars is 50–200 mm), shovel a layer of loose paste into the cathode slot, and tamp manually the paste with a pneumatic ramming machine. The paste in both sides is rammed in five layers. There is a bottom layer of paste about 15 mm thick before placing steel bars for the first four test cells and the related reference cells, and a bottom layer of graphite particles about 5 mm thick for the last two test cells and the related reference cells.

Resistance preheating method of coke bed is used for all test and reference cells. The preheating time is 110 hours, and shunting device is used for the first two days. The initial shunted current is close to 50 %.

All test and reference cells were started up with hot liquid bath and metal was poured after 24 hours. The first CVD measurement takes place about two hours after pouring metal. Then the CVD is measured once per week, and the monthly CVD result is the average of four measurements within the month.

3.3 Test and Reference Cells

Table 3 shows the test and reference cell numbers, super paste for each test cell and starting date of each test and reference cell. All reference cells use Elkem high paste BC20. The side and bottom insulation linings remained unchanged and were the same for all test and reference cells.

Table 3. Test and reference cells: cell number, super paste used, and starting date.

Test cell number	Super paste	Starting date, y-m-d	Reference cell number	Starting date, y-m-d
128	SCP2-2	2024-03-11	204	2024-03-02
435	SCP2-2	2024-03-17	332	2024-03-19
217	SCP2-2	2024-07-23	537	2024-07-10
427	SCP2-2	2024-07-31		
433	SCP2-3	2024-12-01	126	2024-11-09
527	SCP2-3	2024-12-07	603	2024-11-28

3.4 Modelling of CVD and Current Distribution

The CVDs and metal pad horizontal current densities of the first two test cells and reference cells (operation current is 304 kA) are calculated using the Electric Excel Model provided by GeniSim Inc. The result is shown in Table 4. Electrical resistivities of bar pastes BC20 and SCP2-2 at high temperature (about 950 °C) are used.

Table 4. Calculation of horizontal current densities and CVDs of the cathodes rodded with BC20 and SCP2-2 using electric Excel model.

Rodding material	Contact resistivity ($\mu\Omega \cdot m^2$)	Average horizontal current (A/m^2)	CVD1 (mV)	*CVD (mV)
BC20	First assumed	6665	123	176
	First assumed×2	7259	141	194
	First assumed×3	6682	153	206
	First assumed×4	6208	166	219
	First assumed×5	5223	173	226
	First assumed×6	5037	185	238
SCP2-2	First assumed	7133	123	176
	First assumed×2	6535	136	189
	First assumed×3	6074	149	202
	First assumed×4	5863	162	215
	First assumed×5	5235	172	225
	First assumed×6	5158	185	238

*CVD=CVD1+53 (mV)

Please note that CVD1 is calculated by the model and is the voltage drop from the block top to the block end, and there is about another 53 mV voltage drop from the block end to the steel bar end. The first assumed contact resistivity was back calculated with the model according to the CVD measurement result of the first month. The first assumed contact resistivity is the same for the test and reference cells because the initial CVDs are similar. The rest of the contact resistivities were calculated by the first one times 2, 3, 4, 5 or 6.

It can be seen from Table 4 that the current distributions and CVDs of the super paste SCP2-2 and the high paste BC20 are very similar with minor improvement in favour of the super paste. An important influential factor is the contact resistivity. The contact resistivity in an industrial cell varies but generally trend increases with time. The empirical values are used in the Electric Excel model. The contact resistivity when rodding with cast iron is less than that when rodding with a bar paste. How to get a reliable contact resistivity is quite challenging. The contact resistivity can be estimated by CVD measurement in an industrial cell as other parts of CVD like cathode block and steel bar are relatively stable.

3.5 Industrial Trial Result

The preheating and start up process of all test cells went smoothly. The initial voltage in preheating is similar to or about 100 mV higher than that of the reference cells. The increased resistivity of the unbaked super paste did not cause any problems.

3.5.1 CVD Comparison

Figure 3 shows the average CVD developments of the 1st group of two test cells and two reference cells, all test and reference cells were started up in March of 2024.

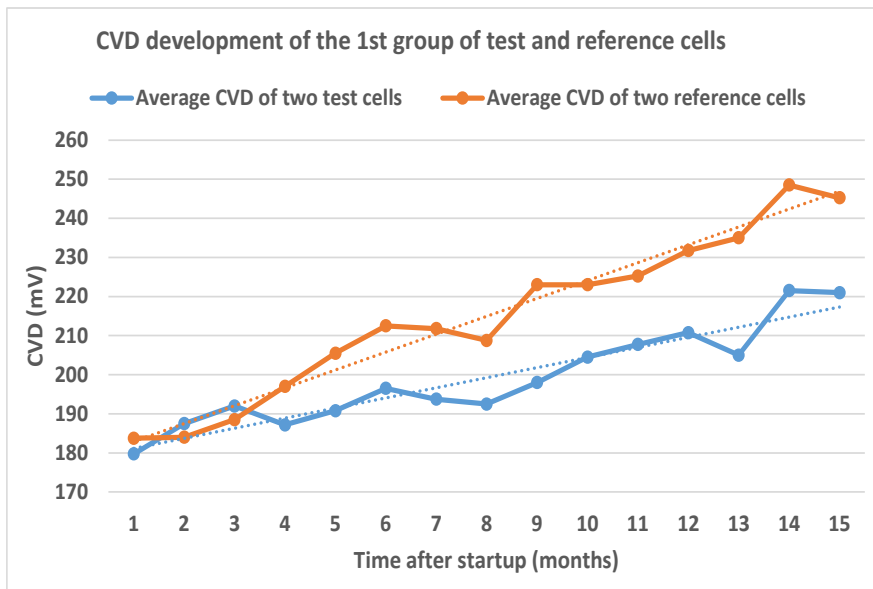


Figure 3. CVD developments of the 1st group of test and reference cells.

It can be seen from Figure 3 that the two average CVDs are quite similar in the first three months, the difference is only 3–5 mV. The average CVD of the two test cells became less than that of the two reference cells from the fourth month and remained less until the end of June of 2025. The grand average difference from the fourth month to the 15th month (July 2024 to June 2025) is 19.8 mV. Please note that all test and reference cells started normal operation and performance evaluation from the fourth month (July 2024).

The CVD measurement results of the 2nd group of test and reference cells are shown in Figure 4. The CVDs of the average of two test cells and one reference cell are similar for the 1st month, the difference is only 2.5 mV. Starting from the 3rd month, the CVD difference is over 10 mV and the grand average difference from the 4th month to the 11th month (November 2024 to June 2025) is 18.3 mV. Comparing the CVD in Figure 4 to the corresponding CVD in Figure 3, it can be seen that both CVDs of test and reference cells of the 2nd group are less than those of the 1st group, and the CVD of the reference cell of the 2nd group is similar to that of the reference cell of the 1st group from the 2nd month to the 7th month, while the average CVD of the two test cells of the 2nd group remained less than that of the two test cells of the 1st group until the 6th month. Starting from the 7th month, the CVDs of the 2nd group are similar to the corresponding CVDs of the 1st group.

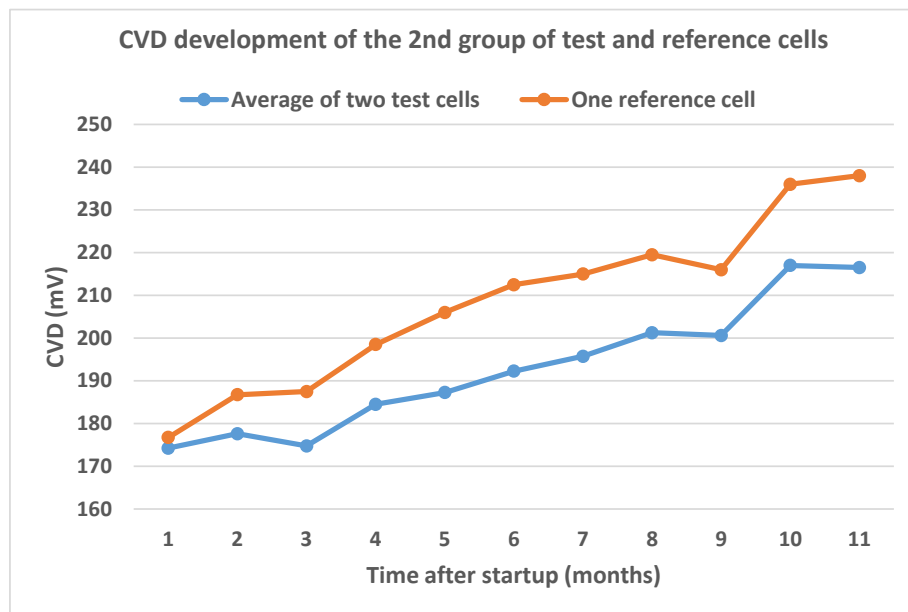


Figure 4. CVD developments of the 2nd group of test and reference cells.

Figure 5 shows the CVD developments of all four individual cells of the 1st group. S in the bracket after the cell number refers to super paste and H high paste. Although the general trends are all increasing with time, the individual developments are quite different, especially the two reference cells, and the four curves have a few intersections. To have a more statistical significance, it seems more test and reference cells are needed.

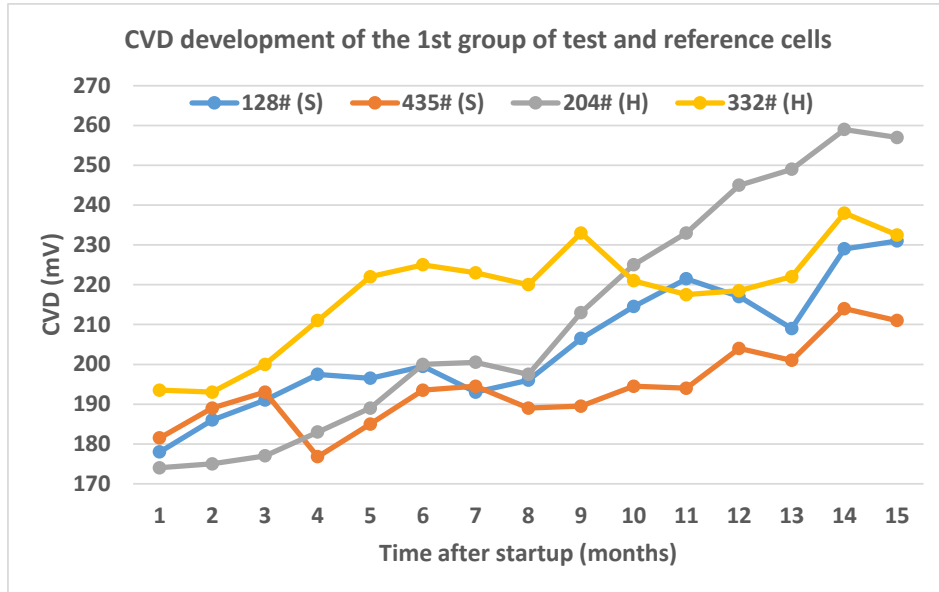


Figure 5. CVD developments of the individual cells of the 1st group.

3.5.2 Current Efficiency and DC Power Consumption

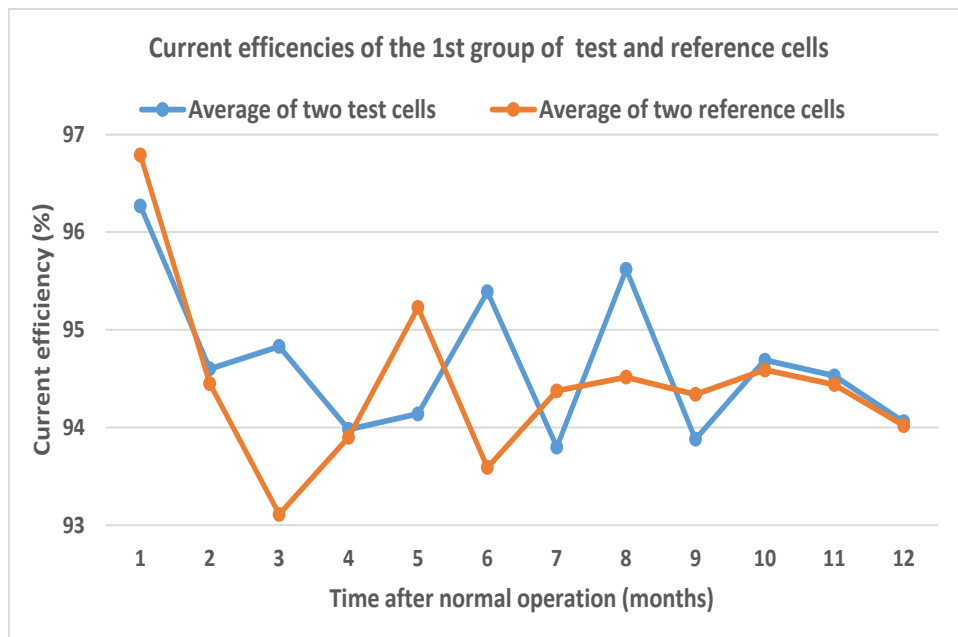


Figure 6. Current efficiency evolution of the 1st group of test and reference cells.

The current efficiencies after normal operation of the first group are shown in Figure 6. The average current efficiencies of the two test cells and the two reference cells are quite similar, the grand average difference after normal operation is 0.20 % with the test cells on the high side. All test and reference cells started normal operation and performance evaluation from July 2025 which is the 1st month in Figure 6 and the 4th month in Figure 3. The current efficiency was calculated according to its definition, i.e.: the actual metal output divided by the theoretical output times 100 % within each calendar month.

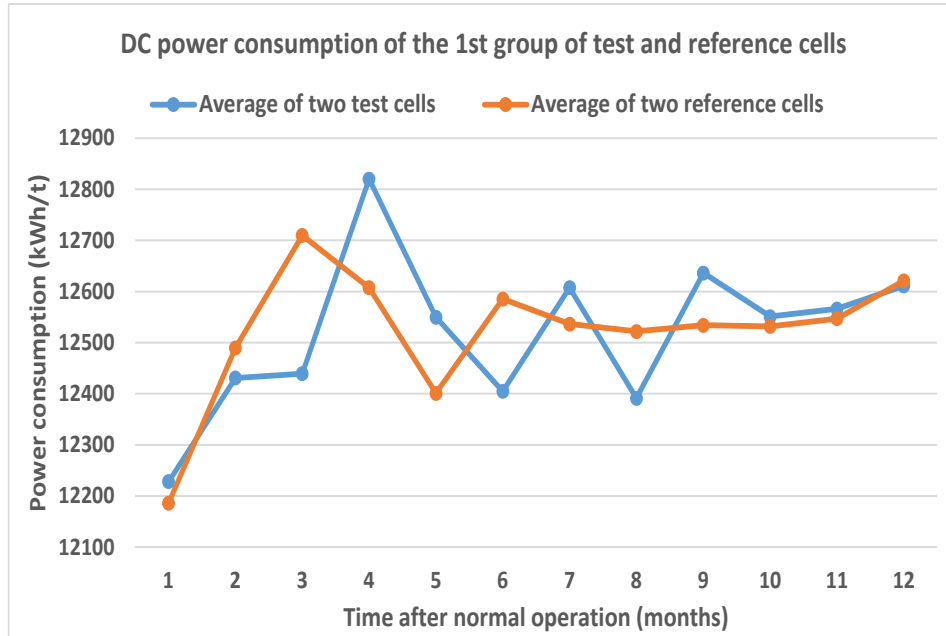


Figure 7. DC power consumption developments of the 1st group of test and reference cells.

The DC power consumptions of the two test cells and the two reference cells of the first group are shown in Figure 7. The consumptions are very similar or roughly the same. The grand average difference after normal operation is only about 3 kWh/t Al. The DC power consumptions were calculated using 2.98 times the cell to cell voltage plus the allocated voltage of anode effects and then divided by the current efficiency within the calendar month.

3.5.3 Discussion

The CVDs of the test cells and the reference cells are similar in the first one to three months and meet the modelling result quite well. The CVD difference increased to over 10 mV after two to four months operation and increased to 20–25 mV after ten to fifteen months operation. The mechanism is probably due to the change of the contact resistivity. The initial contact resistivities of test and reference cells were set the same in the Electric Excel Model, but it seems that the contact resistivity of the test cells increased slower than that of the reference cells, which led the CVD of the test cells increased slower than that of the reference cells. The average CVDs of the test cells and the reference cells of the 1st group after 15 months of operation are 221 mV and 245.3 mV respectively, which corresponds quite well to the modelled CVDs in Table 3 when the contact resistivity is increased to four or five times or increased to over six times of the first assumed respectively. The CVD difference increased almost all the time, the trendline equations are $2.583 \times \text{month} + 178.57$ and $4.573 \times \text{month} + 178.32$ respectively. The starting points are almost the same, but the slope of the reference CVD curve is larger about 1.77 times of that of the test CVD curve.

The main difference between the 1st group and the 2nd group is the reduction of the width ratio of the slot width to the bar width. The slot width of the cathode block of the 2nd group is reduced from 95 mm to 90 mm, making the width ratio reduced from 1.357 to 1.286. The purpose is to increase pressure on the bar paste (the pressure is caused by the bar expansion). It seems that the width change has more effect on the super paste than on the high paste.

It must be pointed out that reducing the width ratio will increase the risk of cracking the cathode block by the steel bar expansion. Widening the steel bar without proportionally widening the cathode slot has been common in recent 20 years in China. The purpose is to reduce CVD and

horizontal current density in the metal pad. Many cell failures have occurred and one of the main mechanisms is cracking of the cathode block by the steel bar expansion.

The current efficiencies and power consumptions of the test cells and the reference cells are very similar with a slight difference in favour of the test cells. This means that the CVD reduction by less than 20 mV does not have significant impact on the current efficiency and the power consumption. The general development trends of the current efficiency of the test and reference cells are similar, and the general development trends of the DC power consumption of the test and reference cells are similar too.

From the energy balance point of view, reduction of CVD alone is just one of the two steps required to reduce cell energy consumption, the other step is reduction of the heat loss by increasing the lining insulation. Since the second step is not performed, the reduction of the CVD needs to be compensated by an increase of ACD (anode-cathode distance) to maintain the cell energy balance, this may lead to a slightly increased current efficiency.

4. Concluding Remarks

The industrial trials of super conductive bar pastes SCP2 are quite successful. The result is promising. The installation is simple and the procedure is the same as that of traditional carbon based cold bar pastes. The first group of two trial cells have been in operation for over one year now. Compared with two reference cells using Elkem high conductive bar paste (high paste), the cathode voltage drops of these two trial cells are on average 19.8 mV lower than that of the two reference cells. The modelled CVDs by Electric Excel Model is improved by using the resistivities of bar pastes at high temperature. The reliable modelled data rely on the appropriate contact resistivities which must be collected from CVD measurements of industrial aluminium cells. The impact of type 2 super pastes on current efficiency and DC power consumption is small, and both indicators have minor improvements or are roughly equivalent. To have more reliable conclusions, more trials are needed.

The super paste has not yet been finalized and is still under continuous improvement. The main recent improvements include a) stronger bonding to the steel bar after baking which is expected to lower the contact resistivity and hence CVD from the very beginning and b) change to a green water-soluble binder without any PAHs or other toxic materials. More industrial trials of super pastes are currently underway or planned, and the trial results will be publicly reported in the future.

5. References

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