Use of Barrier Material to Reduce Sodium Penetration to the Sub-Cathodic Lining of Electrolytic Cells

Shaikha Fatima Almualla[1], Yousef Ahli[2], Ali Jasim[3] and Mohamed Tawfik[4]
1. Senior Superintendent, Cell Design
2. Vice President, Reduction
3. Director, Cell Lining Process Control
4. Manager, Cell Lining Smelting Development
Emirates Global Aluminium, Jebel Ali, Dubai, United Arab Emirates
Corresponding author: falmualla@ega.ae
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Abstract

Cathode block heaving and cracking along the centreline in electrolysis cells have been observed in some EGA cells. These occur due to expansion of cathode blocks and bottom lining as a result of sodium penetration into these materials. The resultant stresses impact cell operation and cell life. The use of a barrier material placed directly underneath the cathode block was tested by EGA as part of cell lining improvements to reduce sodium penetration into the bottom lining. This paper discusses the results of using two potential barrier materials – graphite foil and steel. The conclusions are based on autopsies of two test cells, one for each barrier material.

Keywords: Aluminium reduction cell, Cathode block heaving, Sub-cathodic lining, Barrier materials, Sodium penetration, Cell autopsy.

1. Introduction

The integrity of the potlining materials is a crucial factor in reduction cell performance and operating cost. The cathode block, carbon materials and sub-cathodic refractories undergo extreme conditions during cell life, which affect cell operating condition, cell performance and cell life.

The potlining degradation is a combination of several factors, of which sodium penetration is a crucial mechanism. It can cause cathode block cracking or heaving, leading to potential increase in cathode block resistance, cell instability and early failures.

There have been many attempts to test different materials and design improvements, aiming to reduce the impact of sodium penetration in the reduction cell. EGA has undertaken controlled trials to test different materials as a protective layer underneath the cathode block. The paper discusses the main findings from the test cells using graphite material (Test I) and steel plate (Test II).

1.1 Sodium Penetration Through Potlining Materials

One of the main degradation mechanisms is sodium penetration into sub-cathodic materials as a result of the electrolysis process. Sodium migrates downward through the carbon cathode blocks into the sub-cathodic refractories by electrochemical driving force [1]. Sodium in aluminium will be in equilibrium with the melt species (NaF and AlF_3) as per Equation (1) and react further to sodium in carbon Equation (2) [2, 3].

$$Al_{(l)} + 3NaF_{(in\ cryolite)} \rightleftarrows 3\ Na_{(in\ Al\ )} + AlF_{3\ (in\ cryolite)} \tag{1}$$

$$Na_{(in\ Al)} \rightarrow Na_{(in\ Carbon)} \quad (2)$$

Sodium penetration occurs through the cathode block pores and cracks. It penetrates alumina and silica-based refractory materials and forms sodium aluminate and sodium silicate compounds, which can contribute to significant chemical and mechanical degradation of the lining materials [1, 4]. The increase in sodium penetration is influenced mainly by current density and some other factors, such as bath temperature and composition, and cathode material composition. The result is cathode block expansion and heaving, and degradation of sub-cathodic lining materials. While sodium penetration of the carbon lining materials is normal and unavoidable, excessive penetration may lead to decrease in the thermal insulation and significant contribution to cell failures.

Cracking of cathode blocks is an important factor that adversely affects the cell performance and cell life. Crack formation is mainly due to thermal stress, mechanical stress and electrochemical degradation [1].

Cathode block heaving can cause major disruptions to operations. Heaving occurs due to sodium infiltration and thermal expansion [3]. Sodium expansion of carbon blocks and bath penetration into refractory materials cause cathode block heaving and eventual cracking and spalling. Spalling detaches surface layers of the cathode blocks and exposes them to further erosion and degradation, which compromise the integrity of the entire potlining. Cracking provides infiltration paths for sodium and molten bath to the refractory lining and facilitates chemical attack of refractory lining materials [5].

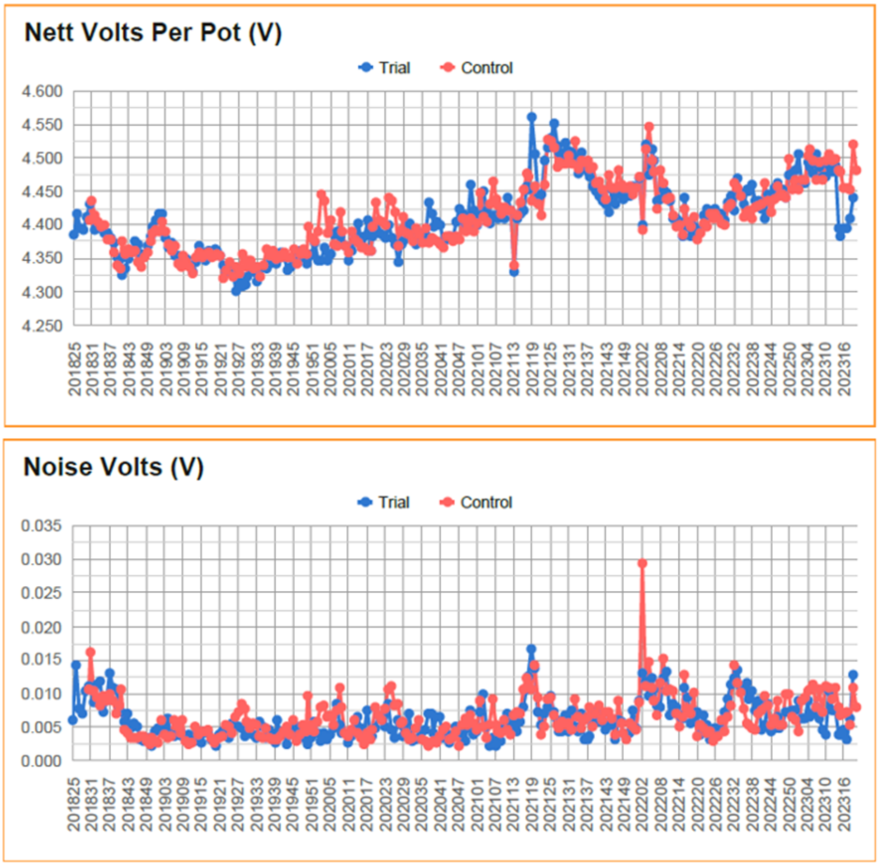
2. Test I: Using Graphite Foil

A controlled test of bottom lining material was conducted at EGA to evaluate the use of graphite foil as a barrier protective layer to stop sodium penetration to sub-cathodic lining materials. A graphite foil of 0.5 mm thickness was used in the test cell. A double layer of the foil was placed on the top of firebricks, under the cathode block, throughout the cell, while keeping other materials with no change. Five test cell were built: three cells in CD20 technology and two in D20 technology.

Figure 1. Cell construction using graphite foil.

2.1 Graphite Foil Performance

The trial cells were monitored closely. Trial cells had smooth operation and did not have any sign of abnormality due to the tested material. The cell performance was compared to control cells with similar cell age and standard lining materials. Figure 2 shows the comparison over 5 years. Table 1 gives average values over the duration of the tests.



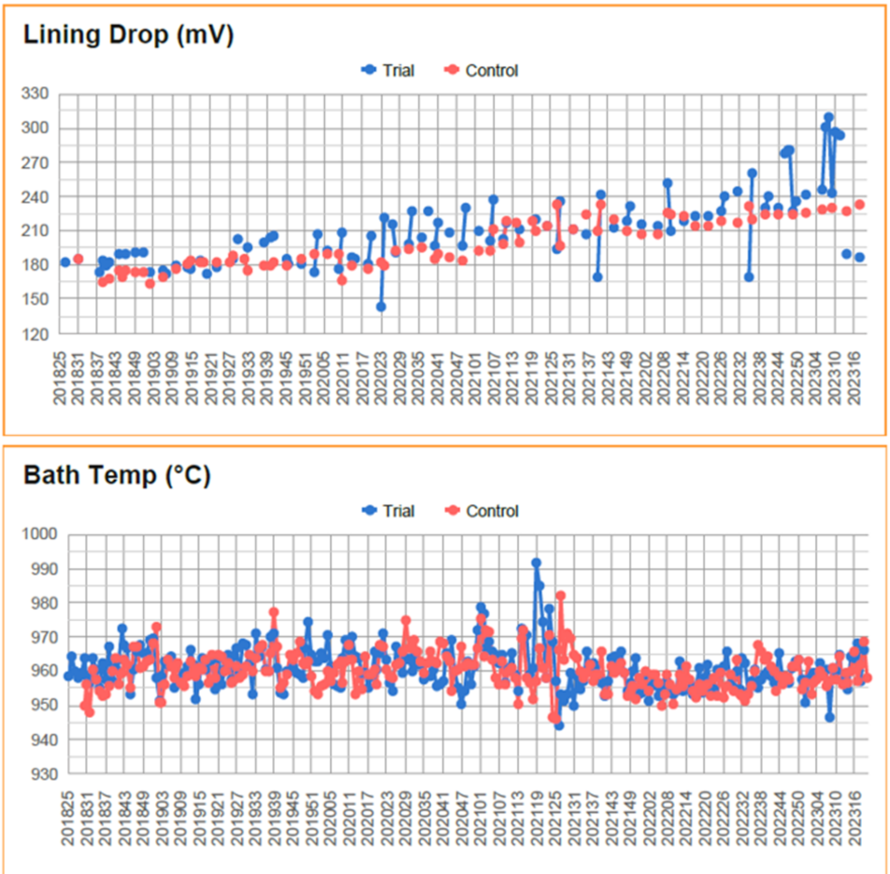


Figure 2. Operational performance trend of trial cells using graphite foil.

The net cell voltage of trial cells was comparable with the control cells. The cathode lining drop was 5–10 mV higher than in control cells, though it was within measurement error. The cell stability was normal with noise and bath temperature similar in test cells and control cells.

Table 1. Summary of average operational data of test cells using graphite foil.

Parameter	Trial	Control	Difference Trial - Control
Amperage (kA)	251.3	252.1	0.2
Net cell voltage (V)	4.408	4.412	-0.004
Noise (V)	0.006	0.006	0.000
Lining drop (mV)	211	198	12
Temperature (°C)	960	960	0

The trial cells were monitored until the end of life to evaluate cell life, and the integrity of the tested material was verified by cavity inspection and autopsy.

2.2 Cavity Inspection of a Graphite Foil Trial Cell

A detailed cell autopsy was made for one trial cell. The selected cell was cutout due to early tap out at 1208 days. The surface cavity inspection showed typical erosion pattern with deepest point measured above collector bar #16 at the upstream location. The cathode surface is shown in Figure 3.

Figure 3. Test I, view of the cathode block surface.

Further inspection was made with cell autopsy. The blocks were removed at several locations to the shell bottom surface to verify the condition of sub-cathodic lining materials (Figures 4 and 5). The effectiveness of the graphite foil material could not be confirmed. The graphite foil was found at a few locations as a thin black layer, but the material was degraded in many places. The sodium penetration occurred through the sub-cathodic materials with the reaction zone boundary at expected location without the foil. The cell had no cathode heaving or major cracks and this was comparable to the control cells with similar lining design.

Figure 4. Test I, slice view (1).

Figure 5. Test I, slice view (2).

Cavity measurements and autopsy slice measurements were made in the tested cell. Figure 6 shows the sub-cathodic profile of materials along a cathode block, across the cell width. It confirms that the cell did not have any heaving since the cathode block bottom location is aligned with the initial construction of the sub-cathodic course of the cell. The middle line shows the boundary of the reaction front. The insulation layer was slightly compressed.

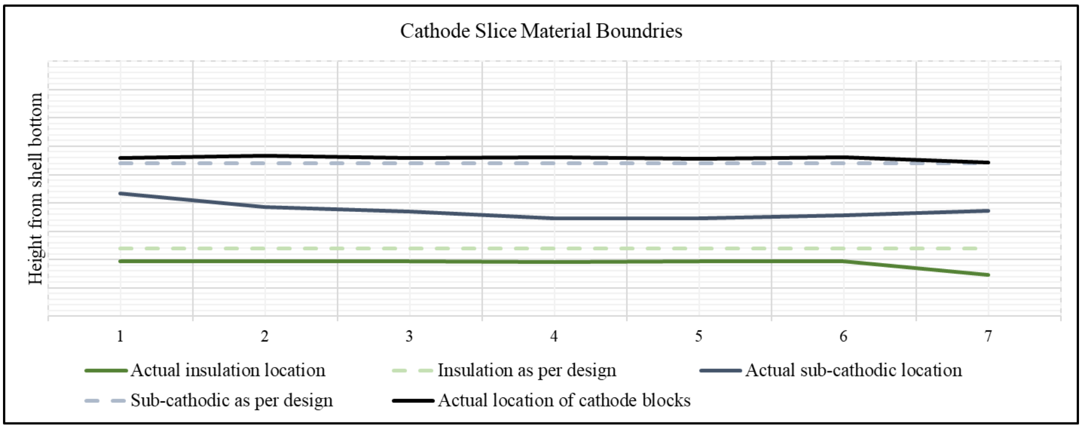


Figure 6. Test I, cathode slice measurements.

Cell life of the trial cells was in the normal range of the implemented technology, with no gain.

3. Test II: Using Steel Plate

Using similar approach as in Test I, a steel plate of 20 mm thickness was installed as barrier layer. Initially, three cells were built and installed in D20 technology. The plate was installed just below cathode blocks on top of the firebrick layer. Figure 7 shows the installed plate.

Figure 7. Cell construction using steel plate

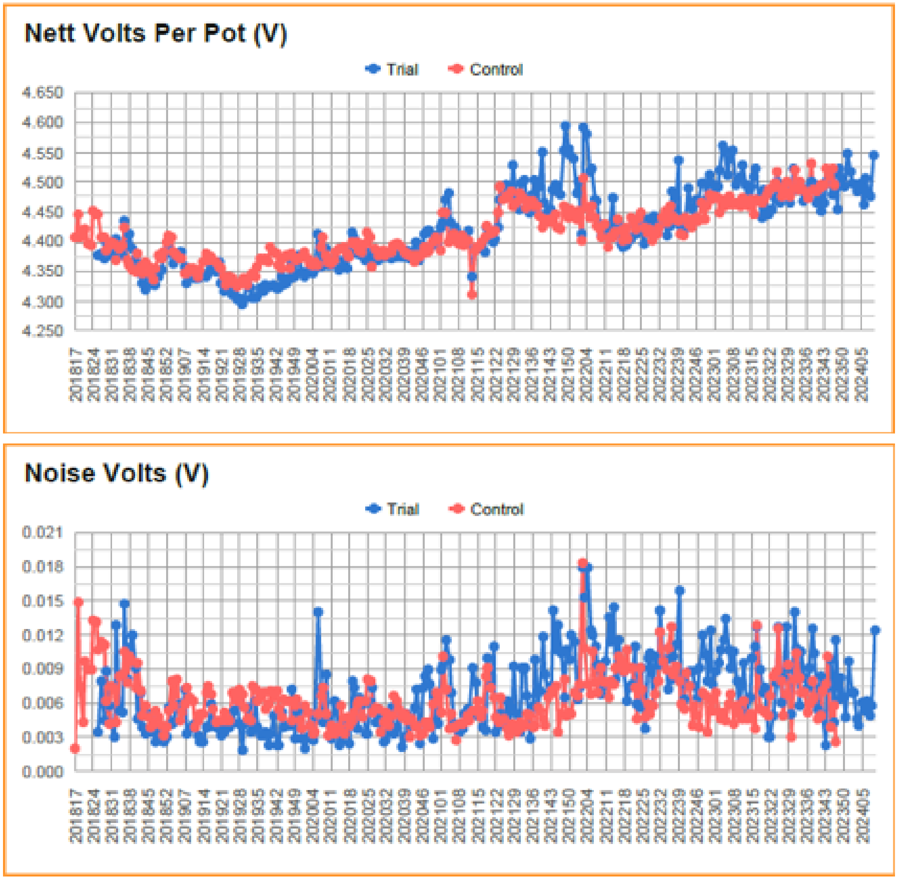
3.1 Steel Plate Performance

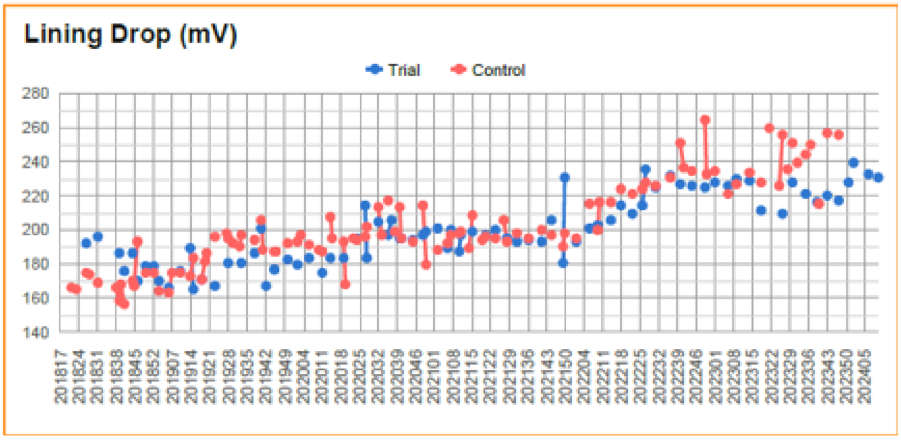
The trial cells were monitored and evaluated through the entire cell life from bath up to failure. The trial cells' current efficiency, specific energy consumption and cathode voltage drop (lining dop) were comparable with control cells. Figure 8 shows the graphs, and Table 2 gives average values.

Table 2. Summary of average operational data of test cells using steel plate.

Parameter	Trial	Reference	Difference: Trial - Control
Amperage (kA)	252.3	252.3	0.0
Net cell voltage (V)	4.416	4.414	0.002
Noise (V)	0.007	0.006	0.001
Cathode voltage drop (mV)	198	202	-4
Temperature (°C)	960	960	0

Overall trial and refence cells were operating with similar operating window and showed similar performance.





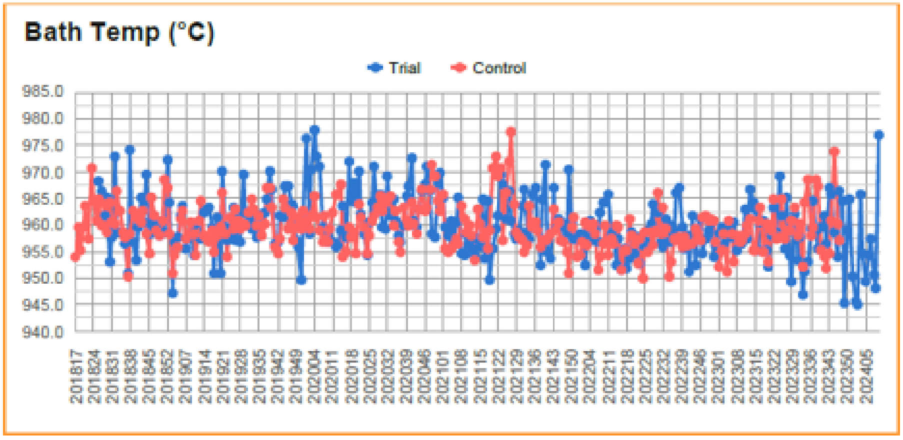


Figure 8. Operational performance trends of trial cells using steel plate.

3.2 Cavity Inspection of a Steel Plate Trial Cell

The cell cavity inspection was made during a power outage at cell age of 972 days. The surface inspection showed no presence of any abnormality and the cavity measurement, including the erosion measurement, was comparable to control cells with similar lining. After the inspection, the cell was restarted.

Figure 9. Test II, view of the cathode block surface at the age of 972 days.

After the restart, the cell failed at age of 1163 days due to iron attack, at a restart age of 191 days. A detailed autopsy was conducted and the steel plate was found in good condition. Minor heaving in the centre of the block was observed and confirmed by measurement.

Figure 10. Steel plate during cell autopsy.

The cell showed abnormal longitudinal cracks along the cathode blocks. The observation was confirmed through the autopsy slice at several locations. Since the steel plate was installed in direct contact with the steel collector bars, it might have caused the bottom of the cathode block to be colder due to higher lateral heat dissipation. This can explain the cell operation with high bath temperature fluctuation seen in Figure 8.

Figure 11. Test II, slice view (1).

The steel plate was effective in stopping the sodium penetration and reaction of the bottom firebricks. Therefore, the sodium reaction layer was found at the steel plate. The sub-cathodic lining materials were unreacted and in good condition.

Figure 12. Test II, slice view (2).

Figure 13. Test II, slice view (3).

Figure 14 shows the sub-cathodic measurements of the autopsied cell. The actual sub-cathodic location exactly matches with the cathode block bottom, which clearly indicates that the reaction zone stops at the cathode block bottom at the steel plate location.

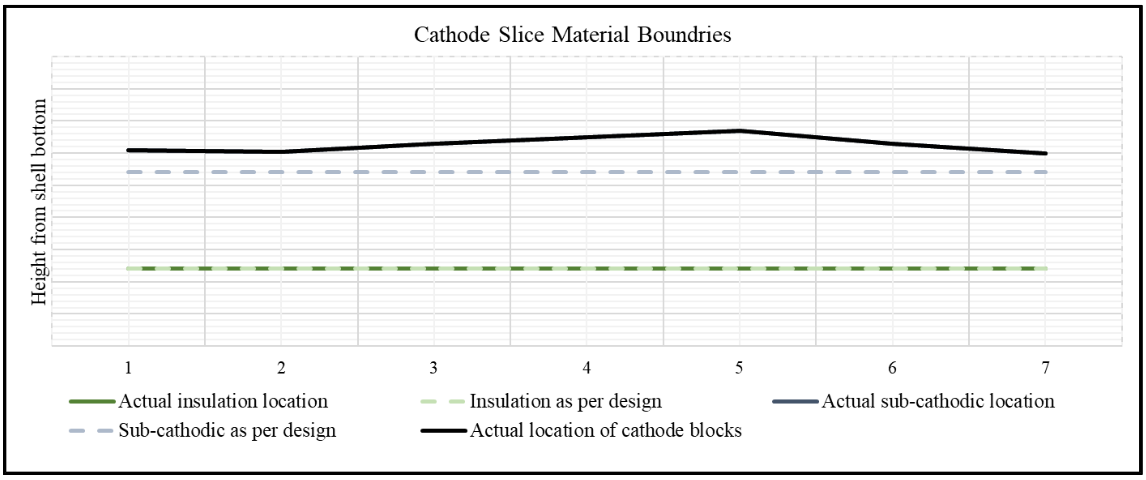


Figure 14. Test II, cross-section measurements.

The tested cells achieved normal cell life in that technology, excluding the restarted cell described here, which was an outlier.

4. Conclusions

Sodium penetration into carbon blocks and bottom lining occurs due to the aluminium electrolysis. Excessive sodium penetration can lead to cathode cracking or major cathode block heaving which can limit the cell life. The paper described testing of two different materials as a possible barrier to sodium penetration:

1) In test I, thin graphite foil under the cathode block did not show any benefit and did not prevent sodium penetration through the sub-cathodic lining.
2) In test II, the steel plate effectively stopped sodium penetration to the sub-cathodic materials. Even though, the cathode voltage drop was nearly the same as in control cells, major cracks in the cathode blocks were observed, but we have no proof that the cracks were related to the presence of the steel plate. Apart from the autopsied cell, which was an outlier, the life of other test cells was in the normal range for that technology. As a result, we believe that a steel plate barrier is a good option for further tests in other cell technologies.

5. References

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