Review of Lining Materials and Their Degradation in Aluminium Electrolysis Cells

Samuel Senanu[1], Egil Skybakmoen[2], Arne Petter Ratvik[3], Zhaohui Wang[4] and Asbjørn Solheim[5]
1, 3. Senior Research Scientists
2. Research Manager
4. Research Scientist
5. Chief Scientist
SINTEF Industry, Trondheim, Norway
Corresponding author: samuel.senanu@sintef.no
https://doi.org/10.71659/icsoba2025-al076

Abstract

The need for high energy efficiency and productivity in modern high-amperage aluminium electrolysis cells gives extreme requirements to the lining materials used in the cells. The sidelining materials need high thermal conductivity, e. g., nitride-bonded silicon carbide blocks have replaced carbon side blocks. They are also thinner to accommodate wider anodes. In addition, the traditional coal tar pitch binder in the ramming paste has been replaced by the so-called eco-friendly and PAH-free binders. At the cathode, the collector bars are currently constructed with copper inserts or even as full copper bars. There is a tendency to use highly graphitised carbon cathode blocks to reduce energy consumption and maintain thermal balance at higher amperages. The high current densities that may result from the high amperages may facilitate the chemical reactions leading to the degradation of lining materials due to the increased activity of sodium. This review paper will attempt to give an overview of the current knowledge about the lining materials and their degradation mechanisms, as reported in the literature.

Keywords: High-amperage cells, Lining materials, Copper collector bars, Graphite cathode blocks, Degradation.

1. Introduction

Aluminium is currently the most produced non-ferrous metal in the world, with annual global production reaching approximately 73 million tonnes in 2024 [1]. The high production volume of aluminium is due to its numerous applications in modern society, owing to important properties that it possesses, such as corrosion resistance, light weight, excellent thermal and electrical conductivities, and the ability to be alloyed with other metals, etc. The production of aluminium occurs through the Hall-Héroult process, which is based on the electrochemical reduction of aluminium oxide in an electrolysis cell at about 960 °C to 970 °C [2]. The electrolysis cell for producing aluminium consists of carbon anodes that conduct electricity as well as heat and are consumed during the production process, a fluoride melt consisting mainly of cryolite that conducts electricity and dissolves alumina, an aluminium metal pad that acts as the electrochemical cathode, a cathode lining consisting of carbon cathode blocks (with different degrees of graphitisation) rodded with collector bars for conducting electricity and ramming paste to fill the joints between the cathode blocks, a refractory lining, insulation materials, and a side wall material. The carbon cathode lining, the refractories, insulations, and side wall materials are usually arranged in a rectangular steel shell that varies from 9 to 18 m long, 3 to 5 m wide and 1 to 1.5 m deep [2]. The operating cavity depth after installation of all lining materials is about 0.4 to 0.5 m [2]. The molten electrolyte and aluminium metal pad are usually kept at a height of 15–20 cm and 10–20 cm, respectively, during the electrolysis process [2, 3]. There are two types of technologies that are based on the design of the carbon anode: prebaked and Søderberg technologies [2, 4]. Figure 1 is a sketch of the electrochemical reduction cell using the prebaked anode technology.

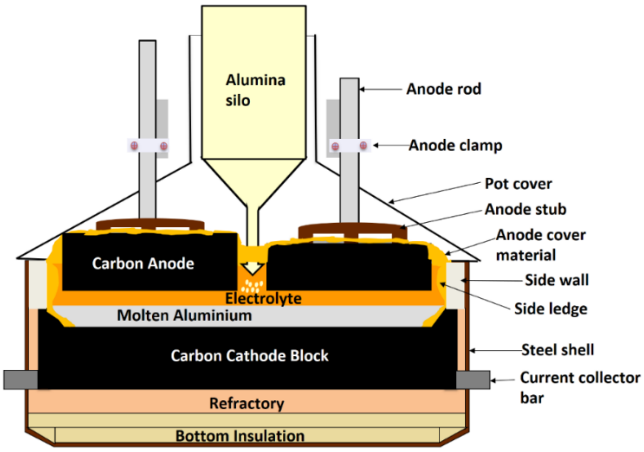

Figure 1. Electrochemical reduction cell using prebaked anode technology [5].

The lining materials within the electrolysis cell will, over time, degrade or, in some extreme conditions, fail, leading to the shutdown of the cell [6]. The time from when an electrolysis cell is started to when it must be decommissioned is referred to as the pot age. The pot age varies a lot and can be from a few hundred days to over 3000 days [7, 8]. The physical and chemical stability of the lining materials varies over time in the electrolysis cell and plays a crucial role in the degradation of the cell lining and consequently the pot life. Owing to the high financial costs relating to building a new cathode lining, loss in production, and disposal of the spent pot lining material after the curtailment, it is imperative to understand the degradation mechanism(s) of the lining materials. This paper presents a review of the different lining materials currently in use in the aluminium electrolysis cells and their degradation mechanism(s).

2. Cathode Lining Materials

2.1 Carbon Cathode Blocks

The use of carbon cathode blocks by the aluminium industry in the construction of the electrolysis cell is due to important properties such as high thermal and electrical conductivity, stability towards molten cryolite and aluminium, mechanical strength, etc. [9]. The carbon cathode blocks used in the aluminium industry are grouped or classified into three main categories, namely graphitised cathode blocks, graphitic cathode blocks and amorphous cathode blocks. The graphitised cathode blocks consist of a graphitizable material (petroleum coke) and binder (coal tar pitch) that have been heat-treated to temperatures reaching 3000 °C, thereby graphitising the whole material. Thus, the graphitised cathode blocks have both the filler and binder content fully graphitised. Some manufacturers impregnate their cathode blocks with pitch before graphitisation to reduce open porosity. Graphitic cathode blocks are made from graphitizable materials such as petroleum coke and/or scrap graphite aggregates, and a coal tar pitch binder. However, the heat treatment is up to ca. 1200 °C, and thus the cathode block is not graphitised as in the case of the graphitised cathode blocks. Amorphous cathode blocks consist of gas or electrocalcined anthracite and a coal tar pitch binder that has been heated to ca. 1200 °C [9]. The high temperature treatment of the filler and binder content of the carbon cathode blocks leads to a higher degree of crystallinity, which is favourable for important properties such as electrical resistivity, especially at temperatures of 2000 °C and above [10]. Table 1 gives some of the important properties of the carbon cathode blocks currently in use in the aluminium industry.

conversion of the whole insulation lining if the refractory lining fails, especially during the early days of operation when the open porosity is free for reactions. Reaction products indicative of aluminothermic reactions, such as $FeAl_2$ and $FeAl_2Si$, have been observed in autopsy samples from the insulation lining, whereas in the worst-case scenario, the whole insulation lining has been replaced by aluminium metal [9]. Aside from the chemical degradation of the insulation lining, these materials are also exposed to high temperatures and compression from the lining materials on top of them. Insulation materials are reported to be dimensionally unstable, experience shrinkage and changes in crystalline structures at higher temperatures [9, 48, 49].

4. Conclusions

The literature studies have shown that extensive work has been done in understanding the cathode lining materials used in the aluminium industry in terms of material properties and degradation mechanisms. The studies reveal that sodium is by far the dominant factor in the degradation of the cathode lining as it partakes in the reduction of materials, including oxides within the refractory and insulation lining, etc. It also paves the way for electrolyte infiltration into the whole cathode lining, thereby kickstarting the fluoride attack of the refractories and insulation lining. Despite the dominant role of sodium in the degradation of the lining, the literature also reports the devastating degradation that occurs if the lining material fails to prevent the rapid infiltration of molten aluminium and cryolite due to cracks or imperfections created due to bad cathode construction procedures. The chemical components chosen for the refractories used in the aluminium electrolysis cells are designed to form effective penetration barriers like albite, to reduce the degradation rates, and thus, proper construction procedures may help to maintain acceptable pot life.

Moreover, the importance of electrochemical and chemical wear relative to physical or mechanical wear of the carbon cathode blocks suggests that a uniform current distribution and calm metal and bath movements are crucial to obtain a relatively uniform wear pattern along the cathode surface that could contribute to higher pot age even as amperages are increased. This is especially true for the highly electrically conducting graphitised cathode blocks due to the peaking of current at the ends of the cathode blocks. The use of copper insert collector bars as well as full copper collector bars may help to even out the current distribution along the cathode block; however, actions need to be taken to prevent the copper from contacting chemical components that could react with it and change its properties. Furthermore, it is crucial to test the lining materials used in the construction of cathode lining to ensure they meet the specifications provided by the suppliers before installing them, as properties such as porosity, density, mechanical and chemical stability play a very important role in determining the rate of the degradation mechanisms.

5. Acknowledgement

The authors wish to express profound gratitude to Dr Morten Sørlie and the late Emeritus Professor Harald A. Øye for their extensive and pioneering contributions to the understanding of cathode lining materials degradation in aluminium electrolysis cells. Their work has laid a critical foundation for ongoing research and advancement in cathode lining materials for the aluminium industry.

6. References

1. International Aluminium Institute website, https://international-aluminium.org/statistics/primary-aluminium-production/ (Accessed on 23 June 2025).
2. Jomar Thonstad et al., *Aluminium electrolysis: Fundamentals of the Hall-Héroult process*, Aluminium-Verlag Marketing and Kommunikation GmbH, 2001.

3. Halvor Kvande and Per Arne Drabløs, The aluminium smelting process and innovative alternative technologies, *Journal of Occupational & Environmental Medicine* 2014, 56, S23–S32. https://doi.org/10.1097/jom.0000000000000062
4. Kai Grjotheim and Harald Kvande, *Introduction to aluminium electrolysis: Understanding the Hall-Héroult process*, Aluminium-Verlag, 1993. https://doi.org/10.1007/978-1-4613-4136-9_23
5. Samuel Senanu, *Cathode Wear in Aluminium Electrolysis Cells*, PhD Thesis, Norwegian University of Science and Technology, 2019. http://hdl.handle.net/11250/2627792.
6. Morten Sørlie and Harald A. Oye, *Cathodes in aluminium electrolysis*, Aluminium-Verlag Marketing & Kommunikation GmbH, 2010.
7. Morten Sørlie, Jan Hvistendahl and Harald A. Øye, Early failure mechanisms in aluminium cell cathodes, *Light Metals* 1993, 299–308, also in *Essential Readings in Light Metals* 2016, 921-930. https://doi.org/10.1007/978-3-319-48200-2_122
8. Samuel Senanu et al., Cathode wear based on autopsy of a shutdown aluminium electrolysis cell, *Light Metals* 2017, 561–570. https://doi.org/10.1007/978-3-319-51541-0_70
9. Morten Sørlie and Harald A. Oye, *Cathodes in aluminium electrolysis*, Aluminium-Verlag Marketing & Kommunikation GmbH, 2010.
10. S. R. Brandtzæg, H. Linga and H. A. Øye, Structural changes in carbon by heat treatment, *Essential Readings in Light Metals* 2016, 754–761. https://doi.org/10.1007/978-3-319-48200-2_99
11. L. Rivoaland, Development of a New Type of Cathode for Aluminium Electrolysis, in: *Proceedings of the 34th International ICSOBA Conference*, 3-6 October 20216, Quebec City, Canada, 2016: *TRAVAUX* 45, 757–765.
12. J.M. Dreyfus and L. Joncourt, Erosion mechanisms in smelters equipped with graphite blocks - a mathematical modeling approach, *Light Metals* 1999, 199–206.
13. Oscar Alberto Vera Garcia1 et al., The robustness of ready-to-use cathodes (RuC®) - a mature technology available for the primary aluminium industry, *Proceedings of 42nd International ICSOBA Conference*, 27-31 October 2024, Lyon, France, *TRAVAUX* 53, 1633–1642. https://doi.org/10.71659/icsoba2024-al050
14. Nadia Ahli et al., EGA experience with full copper cathode collector bars, *Proceedings of 42nd International ICSOBA Conference*, 27-31 October 2024, Lyon, France, *TRAVAUX* 53, 1643-1656. https://doi.org/10.71659/icsoba2024-al051
15. Bénédicte Allard, Mohamed Tawfik and Arvind Kumar, Performances of green and eco-friendly ramming pastes in ega pots, *Metals* 2016, 6(5). https://doi.org/10.3390/met6050112
16. Alexander Arkhipov et al., EGA journey with different ramming pastes, *Light Metals* 2022, 911–920. https://doi.org/10.1007/978-3-030-92529-1_119
17. Andrey Yurkov, *Refractories for aluminium*, Springer International Publishing, 2015. https://doi.org/10.1007/978-3-319-11442-2
18. Egil Skybakmoen et al., Quality evaluation of nitride bonded silicon carbide sidelining materials, *Light Metals* 2005, 773–778. https://doi.org/10.1007/978-3-319-48200-2_114
19. Egil Skybakmoen, Quality evaluation of nitride–bonded sic sidelining materials: historical trends 1997–2022 including results and development of test methods, *Light Metals* 2022, 921–928. https://doi.org/10.1007/978-3-030-92529-1_120
20. Christian Schøning, Tor Grande and Ole-Jacob Siljan, Cathode refractory materials for aluminium reduction cells, *Light Metals* 1999, 231–238. https://doi.org/10.1007/978-3-319-48200-2_112
21. Ole-Jacob Siljan, Christian Schoning and Tor Grande, State-of-the-art alumino-silicate refractories for al electrolysis cells, *JOM* 1997, 295–301.
22. Kati Tschöpe, *Degradation of Cathode Lining in Hall-Héroult Cells*, PhD Thesis, Norwegian University of Science and Technology, 2010.
23. Samuel Senanu et al., Carbon cathode wear in aluminium electrolysis cells, *JOM* 2020, 72(1), 210–217. https://doi.org/10.1007/s11837-019-03717-z

24. Kristin Vasshaug et al., Wear of carbon cathodes in cryolite-alumina melts, *ECS Meeting Abstracts* 2007, 821–826. https://doi.org/10.1149/ma2006-02/45/2011
25. Shinjiro Toda and Tsutomu Wakasa, Improvement of abrasion resistance of graphitized cathode block for aluminium reduction cells, *Light Metals* 2003, 647–653.
26. Xian-an Liao and Harald A. Øye, Physical and chemical wear of carbon cathode materials, *Light Metals* 1998, 667–674, also in *Essential Readings in Light Metals* 2016, 984-991. https://doi.org/10.1007/978-3-319-48200-2_131
27. Siegfried Wilkening, Pierre Reny, Erosion rate testing of graphite cathode materials, *Light Metals* 2004, 597–602.
28. Kati Tschöpe et al., Critical reflections on laboratory wear tests for ranking commercial cathode materials in aluminium cells, *Light Metals* 2013, 1251–1256. https://doi.org/10.1002/9781118663189.ch211
29. R. C. Dorward, Reaction between aluminum and graphite in the presence of cryolite, *Metallurgical Transactions* 1973, 4(1), 386–388.
30. B. Novak et al., Fundamentals of aluminium carbide formation, *Light Metals* 2012, 1343–1348. https://doi.org/10.1007/978-3-319-48179-1_232
31. Samuel Senanu et al., Wetting of carbon cathodes by molten electrolyte and aluminium, *Light Metals* 2021, 699–707. https://doi.org/10.1007/978-3-030-65396-5_92
32. N. Eustathopoulos et al., The wetting of carbon by aluminium and aluminium alloys, *Journal of Materials Science* 1974, 9(8), 1233–1242. https://doi.org/10.1007/bf00551836
33. R. Ødegard, A. Sterten and J. Thonstad, On the solubility of aluminum in cryolitic melts, *Metallurgical Transactions B* 1988, 19(3), 449–457.
34. K. Vasshaug, *The influence of the formation and dissolution of aluminium carbide on the cathode wear in aluminium electrolysis cells*, PhD Thesis, Norwegian University of Science and Technology, 2008.
35. R. Keller, J. W. Burgman and P. J. Sides, Electrochemical reactions in the Hall-Héroult cathode, *Journal of Metals* 1987, 39(10), A43.
36. Alton T. Tabereaux et al., Erosion of cathode blocks in 180 kA prebake cells, *Light Metals* 1999, 187–192. https://doi.org/10.1007/978-3-319-48200-2_133
37. Pierre Reny and Siegfried Wilkening, Graphite cathode wear study at Alouette, *Light Metals* 2000, 399–404. https://doi.org/10.1007/978-3-319-48200-2_134
38. Pretesh Patel, Margaret Hyland and Frank Hiltmann, Influence of internal cathode structure on behavior during electrolysis Part II: porosity and wear mechanisms in graphitized cathode material, *Light Metals* 2005, 757–762. https://doi.org/10.1007/978-3-319-48200-2_136
39. Kati Tschöpe et al., Electrochemical wear of carbon cathodes in electrowinning of aluminum, *JOM* 2013, 65(11), 1403–1410. https://doi.org/10.1007/s11837-013-0605-4
40. H. Gudbrandsen, A. Sterten and R. Odegard, Cathodic dissolution of carbon in cryolitic melts, *Light Metals* 1992, 521–528.
41. Z. Wang et al., Cathode wear in electrowinning of aluminum investigated by a laboratory test cell, *Light Metals* 2016, 897–902. https://doi.org/10.1002/9781119274780.ch151
42. Bente M. Faaness et al., Ramming paste related failures in cathode linings, *Light Metals* 2016, 827–833. https://doi.org/10.1007/978-3-319-48200-2_109
43. Eirik Hagen, Mari-Ann Einarsrud and Tor Grande, Chemical stability of ceramic sidelinings in Hall-Héroult cells, *Light Metals* 2001, 257–263.
44. Zhaohui Wang, Aging of Si_3N_4-bonded SiC sidewall materials in Hall-Héroult cells, PhD Thesis, *Norwegian University of Science and Technology*, 2010.
45. Wei Gao, A. Hendry and G. Holling, Oxidation of nitride bonded silicon carbide in wet air atmosphere, *British Ceramic Transactions* 2002, 101(6), 231–236. https://doi.org/10.1179/096797802225004027
46. Egil Skybakmoen, Henrik Gudbrandsen and L.I. Stoen, Chemical resistance of sidelining materials based on sic and carbon in cryolitic melts - a laboratory study, *Light Metals* 1999, 215–222.

47. Ole-Jacob Siljan, Christian Schøning and Tor Grande, State-of-the-art alumino-silicate refractories for al electrolysis cells, *JOM* 2002, 54(5), 46–55. https://doi.org/10.1007/bf02701697
48. Ove Paulsen et al., Aging of insulating linings in aluminium electrolysis cells, *Light Metals* 2017, 551–559. https://doi.org/10.1007/978-3-319-51541-0_69
49. Raymond Luneng et al., Chemical stability of thermal insulating materials in sodium vapour environment, *Light Metals* 2017, 543–549. https://doi.org/10.1007/978-3-319-51541-0_68