Study and Judgement on the Technological Dilemma and Trend of Three-Layer Liquid Electrolysis of Refined Aluminium

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Abstract

Three-layer liquid electrolysis, a century-old high purity aluminium production technology, still retains a certain proportion in countries such as Norway, Japan, China and Russia. However, under the immense pressure of emission reduction and energy consumption cost competition, caused mainly by recent-year excess refined aluminium production capacity and trade barriers between countries, it seems to have become an industry consensus that this increasingly niched process will be completely replaced by other purification processes – the segregation method, which has significant advantages in energy saving, environmental protection and broad-spectrum product applicability. Based on a comprehensive comparison and analysis of the strengths and weaknesses between these two, this article proposes feasible paths for breakthroughs and enhancements of industrial competitiveness of the three-layer liquid electrolysis process from the perspectives of process improvement, product upgrading, advantageous industrial chain combinations, and technological innovation.

Keywords: High purity aluminium, Refined aluminium, Three-layer liquid electrolysis, Segregation method.

1. Introduction: Definition, Production Capacity, and Applications of Refined Aluminium

In China, refined aluminium is customarily classified under the category of high purity aluminium. According to the Chinese Nonferrous Metals Industry Standard [1], aluminium with a purity ranging from 99.90 % to 99.996 % (corresponding to grades 3N0 to 4N6) is designated as refined aluminium. This classification aligns respectively with the definitions of high purity and ultrahigh purity aluminium in the American standards – -Grade 1 and Grade 2 aluminium in the Japanese standards, and high purity aluminium under the Russian standards [2].

The global annual production capacity of refined aluminium has currently reached approximately 330 000 tonnes, excluding 3N aluminium products directly manufactured from conventional aluminium electrolysis cells. Major production regions include China, Japan, North America, Norway and Russia. After decades of technology introduction, assimilation, and independent innovation, China's refined aluminium industry has achieved significant growth, with an annual production capacity rising from less than 10 000 t at the beginning of this century [3] to nearly 201 500 t presently (see Table 1).

Approximately 80 % of the refined aluminium is used to produce aluminium foil for electrolytic capacitors. About 10 % is utilized in the manufacture of new energy battery electrodes, hydrogen energy storage and transportation tanks, high-performance conductive wire, cryogenic electromagnetic components, magnetic levitation materials, advanced packaging and coating materials, as well as special aluminium alloys for aerospace and military applications [4]. The remaining 10 % is used for further purification into high and ultrahigh purity aluminium.

Table 1. Changes in China's refined aluminium production capacity over the past 20 years (excluding 3N aluminium produced directly from conventional electrolytic cells).

Purification process	Company	Completed production capacity (kt/y)	Capacity under construction (kt/y)	Potline current (kA)	Year of commissioning	Operational status
Three-Layer Liquid Electrolysis	Guizhou Aluminium Plant	5.5		60	2003	Closed in 2005
	Xinjiang Joinworld Co., Ltd.	5		65	2003	Closed in 2008
		12		80	2005	Closed in 2022
		15		100	2023	Exists
	Shanxi Guan Aluminium Group Co., Ltd.	12		70	2008	Closed in 2009
	Inner Mongolia XinChangjiang Mining Investment Co., Ltd.	10		60	2011	Closed in 2021
	Inner Mongolia Huomei Hongjun Aluminium & Electricity Co., Ltd.	12		80	2008	Closed in 2014
	Yidu Dongyangguang Industrial Development Co., Ltd.	5		60	2003	Closed in 2017
	Qinghai Qiaotou Aluminium and Electricity Co., Ltd.	20		70	2010	Closed in 2015
	Henan Shenhuo Group Co., Ltd.	10		80	2005	Closed in 2016
	Baotou Aluminium Co., Ltd.	3.5	3.5	105	2025	Exists
Segregation method	Baotou Aluminium Co., Ltd	60		--	2007–2022	Exists
	Xinjiang Joinworld Co., Ltd	40		--	2008–2013	Exists
	Tianshan Aluminium Group Co., Ltd.	40	60	--	2023	Exists
	Guangxi Zhengrun New Material Technology Co., Ltd.	5		--	2016	Exists
	Guangxi Laibin Guangtou Yinhai Aluminium Co., Ltd.	10		--	2024	Exists
	Guangyuan Huabo Precision Aluminium Technology Co., Ltd.	20		--	2024	Exists
	Nanshan Aluminium Co., Ltd.	8		--	2024	Exists
	Inner Mongolia Chuangyin New Materials Co., Ltd.	--	50	--	Put into operation by 2026	Exists
	Jili BaiMine Group Co., Ltd.	10		--	2023	Exists
	Tongchuan Aluminium-based New Material Co., Ltd.	--	30	--	Put into operation by 2026	Exists

2. The Industrial Predicament Faced by the Three-Layer Liquid Electrolytic Refined Aluminium Production Process

Three types of processes can be employed to produce refined aluminium of different grade: First, conventional electrolytic aluminium plants, utilizing high-grade alumina, anodes, and fluoride salts as electrolytic raw materials, combined with optimized equipment and process control, enable the direct production of 3N0-3N5 raw aluminium which is purified via transfer pots or furnaces treatments and then cast into refined aluminium ingots for sale. Second, 2N raw aluminium can be purified to 4N to 4N6 grades through a three-layer molten salt electrolytic cell. Third, the segregation method is applied to refine 2N or 3N raw aluminium into 3N5-4N6 aluminium.

Since the 1980s, the three-layer electrolytic refining process, which had dominated the industry for decades [5], has gradually been replaced by the segregation method [6] with large-scale refined aluminium production mainly including stepwise crystallization processes [7] and rotary crystallization techniques [8]. This shift is particularly pronounced in China, primarily due to the overcapacity in refined aluminium investments over the past two decades, the intensifying tariff wars among major producing countries in recent years, increasing tightened domestic regulations on high energy consumption and high emission projects [9], and the upcoming implementation of the European Union's Carbon Border Adjustment Mechanism (CBAM). These factors have adversely affected refined aluminium products, especially those produced via the three-layer process. Currently, apart from a capacity of 15 000 tonnes in Xinjiang Joinworld Co., Ltd [10] and Baotou Aluminium Company's newly built 3000-tonne capacity, a cumulative capacity of nearly 100 000 tonnes of three-layer electrolytic refining aluminium in China has been shut down, suspended, or replaced by segregation process technology (see Table 1). Consequently, the industry participants are questioning whether this century-old refining method [11] will completely disappear, while are also exploring feasible pathways for its coexistence with alternative technologies.

3. Comparison Between Three-Layer electrolysis and Segregation Processes

3.1 Scope and Efficiency of Impurity Removal

The three-layer electrorefining process purifies aluminium by exploiting the difference of deposition potentials between aluminium and other elements under specific electrolysis conditions such as anode current density, electrode distance, composition of molten salt and anode alloy, etc. It offers a wider impurity element removal range than the segregation method, particularly for elements difficult to eliminate by the segregation method with high equilibrium distribution coefficients such as Ti, Cr, Mn, V and Zr. The average separation removal rate for these elements is between 20 to 70 %, while the three-layer electrolysis removal efficiency can reach up to 99.5 % [12].

3.2 Feedstock Adaptability

Theoretically, both the three-layer liquid electrolysis method and the separation process can use different grades of aluminium as raw materials to produce higher-grade aluminium. However, for the three-layer liquid process, using aluminium with higher purity as raw material requires higher purity of the electrolyte and anode alloy elements, and the power consumption cost is higher. Therefore, for the production of aluminium with a purity higher than 5N, its efficiency and cost are difficult to match those of the segregation method. Well for the single-round production of 4N refined aluminium, the three-layer electrorefining process can use 2N-grade aluminium as the feedstock to directly produce 4N to 4N6-grade aluminium (with some cells achieving up to 4N8 to 5N) [13]. In contrast, the single-round segregation method requires 3N-grade raw aluminium, and its segregation products rarely exceed 4N6 grade.

3.3 Product Yield and Quality Improvement

The one-time yield of 4N and above aluminium refined by the segregation method is 65–70 %, with elements of low distribution coefficients such as Fe, Si, Cu, and Mg accumulating in the residual liquid, causing the grade of the remaining aluminium drop below 3N and making its secondary segregation impossible to reach 4N level. In contrast, the one-time yield of 4N and above refined aluminium produced by the three-layer electrorefining process can reach 95-98 %.

Theoretically, the purity of the product can be continuously improved through cyclic electrolysis in the three-layer electrorefining process. However, due to the significant increase in energy consumption and the decreasing impurity removal efficiency with successive electrolysis cycles, to produce high and ultrahigh purity aluminium, some tend to adopt a combined method [12] using the three-layer liquid electrolytic refined aluminium as segregation raw material. This approach requires that the three-layer electrorefining cells steadily yield higher level refined aluminium (4N6-4N8, or even 5N grade). The limiting factors include: (1) melt contamination introduced by corrosion of the cell lining and cathode/anode materials; (2) process disturbances caused by frequent adjustment of electrolyte and anode alloy due to their consumption and composition deterioration by the-generation of cathode slags and anode mud; (4) insufficient plant enclosure and purification conditions.

3.4 Processing Time

Compared to the segregation method, the three-layer liquid electrorefining process requires no pre-treatment of the raw material (involving boriding sedimentation to remove Ti, V, etc., usually taking 8-10 hours) and eliminates the need for solid-liquid separation, sawing, and remelting of raw ingots after segregation refining. As a result, the total process time – from raw material to ingot product casting – can be reduced by 30 % to 40 %.

3.5 Process Energy Consumption

Nearly 95% of the energy consumption of the three-layer liquid electrolysis process is attributed to the electrolysis stage. The electrochemical migration of elements during the electrorefining process itself does not consume electrical energy [14], and no anode effect occurs like the ordinary aluminium electrolysis process [15]. However, due to the presence of concentration polarization overvoltage at both anode and cathode, the high cell voltage required to maintain thermal balance and prevent melt inter-layer mixing (with an polar distance of 8–12 cm), the resistive voltage drops in non-molten conductors inside and outside the cell, electricity consumption during roasting and startup for new cells, as well as cell voltage disturbances caused by electrode replacement and cleaning, the electricity consumption per tonne of aluminium remains 7 to 8 times higher than that of the segregation method (power consumption mainly for furnace insulation and raw ingot remelting) [5, 14]. Although some new large-cell designs have reduced the specific electricity consumption from 17 500–18 600 kWh/t Al at the beginning of this century [3] to the current range of 11 000–13 000 kWh/t Al [14, 16], there remains significant potential for energy savings.

3.6 Automated and Precise Control

The segregation refining process can be precisely controlled through key parameters such as melt temperature and crystal thickness, with minimal human interference. In contrast, three-layer liquid electrorefining process involves frequent disturbances to critical parameters (including melt composition, melt temperature, melt level, and electrode spacing etc.) due to operations such as aluminium addition, electrode cleaning and replacement, bottom sediment and crust removal, and replacement of aged electrolyte and anode alloys. Some of these operations highly depend on the operator's skill level, and even require full cell series power shutdowns, making automation and intelligent control highly challenging. Improper operational experience can easily lead to melt layer mixing, slag shielding, and localized short circuits, causing physical field imbalances and parameter instability, which in severe cases can result in melt spoilage and cell shutdown. With cell capacity gradually increased and stringent restrictions drown to energy consumption and pollutant emissions, achieving precise, reliable automated and intelligent control is imperative.

3.7 Environmental Impact

Apart from the raw material pre-treatment and the remelting and casting processes, which generate a small amount of dust and aluminium slag, the segregation refining furnace itself produces virtually no waste or carbon emissions. As for three-layer electrorefining process, although there are not large emission of anode gases and fluoride salt volatiles as conventional aluminium electrolysis cells do, it still generates much process-related hazardous wastes including hydrolysis and volatilization products from electrolyte molten salt, cathode complexing slags, anode alloy slags, spent electrolyte, and overhaul residues. Moreover, many operations must be conducted at high-temperature, resulting in harsh working environments.

4. Improvement Approaches for the Three-Layer Electrorefining Process

The above process comparison indicates that although the three-layer electrorefining method has advantages in impurity removal scope and efficiency, feedstock adaptability, product grade and yield, and processing time, it faces disadvantages in automated precise control, environmental impact, and more critically in the decisive cost factor – specific electricity consumption per tonne of refined aluminium. To overcome these challenges, simultaneous efforts are required to substantially reduce the energy consumption gap, upgrade product purity, and optimize the integration of upstream and downstream industries.

4.1 Process Performance Improving

4.1.1 Development of High-Conductivity, Anti-Aging, and Environmentally Friendly Electrolyte Systems

Compared with conventional aluminium electrolysis cells, the three-layer electrorefining process utilizes two types of electrolytes – fluoride-based and fluoro-chloride-based systems – which, due to the absence of Al_2O_3 and the addition of barium and lithium salts, exhibit significantly lower electrolyte liquidus temperatures and resistivities [15]. However, the aforementioned advantages result in no remarkable energy savings. Factors, such as melt fluidity and stability, electrode spacing, slag interfacial tension, wettability between anode alloy and carbon brick, and interlayer resistance between electrolyte and anode alloy and refined aluminium, all significantly affect cell power consumption. Therefore, in-depth studies on the mechanisms of melt aging and loss, the morphology of sludge action, and pre-purification mechanism of the mother electrolytic cell are imperative to develop new type of energy-saving and environmentally friendly electrolytes with excellent electrical conductivity compositional stability, and low electrode spacing.

4.1.2 Establishment of a Stable Process Operating Environment

Through multi-physics coupling simulation and optimization involving thermal, electrical, mechanical, magnetic, and fluid dynamic fields, the structure of cell lining and design of the busbar around the cell are improved to maintain a good thermal balance and long-term magnetic stability. This is key to reduce energy consumption, magnetic field gradient in the melt and interface fluctuation deformation, to improve the electrode distance, and to reduce the bottom voltage drop and horizontal current loss in large-capacity three-layer liquid electrolytic cells. Several mature technologies from conventional aluminium electrolysis cells can be referenced in this regard, such as novel energy-saving composite cathode structures [17] and advanced cathode current stabilization and insulation techniques [18, 19]. Additionally, conducting comprehensive multi-physics parameter testing and validation on production cells (formerly known as three-field testing [20]) is also a technical gap that needs to be filled for three-layer electrolysis cells.

4.1.3 Enhancing the Automation and Intelligence Level of Electrolytic Process Control

To improve control on three-layer liquid electrolytic cells, it is necessary to develop an adaptive intelligent cell control system combining local operation with remote visual online monitoring, and integrating multiple control from automatic aluminium feeding, anode changing, to high-efficiency gas collection. Technologies like synchronized short-circuit prevention equipment, anti-short-circuit continuous aluminium stirring and feeding devices for the material chamber [21], integrated temperature control systems for roasting startup [22], uninterruptible refined aluminium extraction and cathode changing in large-cell series [23], and cathodic anti-arc drive system, etc. [24] should be given priority for developments.

4.1.4 Extending Cell Lifespan

Extending the cell lifespan can increase aluminium production and reduce the cost associated with busbar current losses and roasting startups. This depends on both the cell lining design, which provide protection against thermal stress damage and molten metal erosion, and the roasting and startup procedures along with daily operational protocols. Most domestic cell types have been decommissioned before completing a full operational cycle, resulting in a lack of research on cell lifespan, including studies on secondary startup cells.

4.2 Product Grade Improvement

Currently, many enterprises use combined processes [12] to produce ultrahigh purity aluminium (above 5N), hoping for getting aluminium above 4N8 from three-layer electrolysis cells to feed the next segregation process. Due to the inherent energy consumption limitations of the three-layer electrorefining process, there is no way to achieve product grade upgrading through cyclic electrolysis. However, by developing new cell lining and electrode materials, and by improving raw material purity as well as enhancing plant cleanliness conditions, higher-grade aluminium can be produced through one-step electrolysis. In fact, companies such as Sumitomo Chemical and Xinjiang Joinworld Co., Ltd have already produced 5N-grade aluminium in their optimized three-layer electrorefining cells.

4.2.1 Development of Novel Corrosion-Resistant Cell Linings and Electrodes

The sidewalls of three-layer liquid electrolysis cells generally use dense sintered magnesia bricks, which exhibit poor thermal shock stability and are easily corroded and damaged by the electrolyte molten salt. This results in the deposition of impurities such as magnesium and silicon at the cathode. Therefore, it is necessary to develop alternative materials with excellent corrosion resistance, high thermal shock resistance, low thermal expansion, and high thermal plasticity. Examples include spinel bricks with graded porosity structures, resin-bonded magnesia-carbon bricks, and boron nitride composite bricks. The cathode and anode block, mainly high purity graphite-based, can be coated with highly conductive, wear-resistant composite coatings, and for the cell bottom, heat preservation materials of anti-sintering and anti-seepage have good application prospect.

Currently cathodes either refined aluminium-based or graphite-based, suffer from issues such as easy arcing, oxidation, slag formation, and contamination. The adoption of composite cathodes is a promising approach to address these problems. For example, the plasma-sprayed composite coatings of "titanium boride-molybdenum silicide-tungsten silicide" on graphite or cast-iron-based cathodes, invented by Lu Huimin [25, 26], can replace the solid refined aluminium cathodes in fluoride-chloride electrolyte cells , or reduce the consumption of graphite cathodes in fluoride electrolyte cells, by preventing cathode arcing and short circuits, ensuring the stable quality of deposited refined aluminium. Similarly, Lei Zhao et al. [27] invented aluminium-graphite composite cathodes that use commercial aluminium instead of refined aluminium, which lowers consumption costs, extends service life, resists cathode and electrolyte adhesion, and significantly reduces arcing and short-circuit occurrences.

4.2.2 Improving Raw Material and Electrolyte Quality

High purity electrolytes and Al-Cu anode alloys with fewer impurities should be employed to improve the final product quality. Measures like root-cell pre-electrolysis, anode alloy and electrolyte composition online monitoring technology, and waste anode alloy recycling technology can effectively reduce the creation of anode slime and cathode slag. However, the potential increase in cost must be comprehensively evaluated to balance the benefits.

4.2.3 Improving Plant Cleanliness Conditions

The production of high purity materials often requires stringent cleanliness conditions [28, 29]. In three-layer liquid electrolysis, frequent manual operations, such as electrode replacement, aluminium addition and removal and slag cleaning, compromise the sealing of the electrolytic cells, resulting in significant emissions of dust, fume and heat into the plant environment. Relying solely on a fully enclosed fresh air ventilation system to maintain a dust-free workshop entails substantial investment and operating costs. Therefore, apart from optimizing plant's dust-barrier and heat-dissipation structure, it is essential to reduce unorganized cell emissions of fumes and heat through efficient gas collection and purification system design and adoption of intelligent, low-labour operational controls.

4.3 Advantages of Industrial Chain Integration

4.3.1 Upstream Integration

From the perspective of energy supply, three-layer liquid electrolysis production line in Europe, North America, and Russia is typically coupled with low-cost hydropower and renewable energy sources. In China, the operations in regions such as Xinjiang and Inner Mongolia are similarly supported by inexpensive self-supplied electricity, either from renewable energy, or from low-cost coal resources.

From the perspective of raw material acquisition, the 2N-grade aluminium ingots used in three-layer electrolysis (with some operations attempting to feed directly primary liquid aluminium into the refining cells) are mostly sourced from self-owned conventional aluminium smelters. In order to reduce capital investment and management costs, some companies even experimented inserting three-layer refining cells directly into conventional aluminium electrolysis series.

4.3.2 Downstream Integration

The global total current production capacity of refined aluminium via three-layer liquid electrolysis is 66.5 kt now (see Table 2), accounting for only 21.9 % of the total refined aluminium production capacity. Moreover, most of this capacity must be combined with segregation processes to offset energy costs through the production of higher-value end products.

Table 2. Global distribution of refined aluminium production capacity via three-layer liquid electrolysis.(excluding 3N aluminium produced directly from conventional electrolytic cells).

Country	**Total refined aluminium production capacity (kt/y)**	**Three-layer liquid refined aluminium production capacity (kt/y)**
China	201.5	18.5
Norway	8.5	8
Japan	50	15
Russia	15	15
Other regions	28.5	10
Total	**303.5**	**66.5**

With the growing demand for high and ultrahigh purity aluminium (5N and above) in sectors such as high-end integrated circuit target materials, aerospace, and defense, improving the efficiency of impurity element removal has become a key research focus. Sole reliance on multiple rounds of electrolysis or segregation each faces insurmountable challenges in terms of either technical complexity or cost. Emerging technologies such as electromagnetic separation [30, 31], vacuum distillation [32], and organic electrolysis [33] remain under laboratory research and development, and some are to enter the industrialization stage. Therefore, joint purification process, which combines three-layer electrolysis with segregation or other purification methods, may offer strong complementarity, and has emerged as the preferred approach for the large-scale production of high and ultrahigh purity aluminium. When this process integration is coupled with renewable energy sources or downstream deep-processing industries, its competitive advantages will become even more pronounced.

5. Technological Innovations and Applications for Three-Layer Liquid Electrolysis

5.1 Development of Small-Scale Varietal Electrolysis Cells

Over the past decades, the capacity and control precision of three-layer liquid electrolysis cells have continuously improved. Today, the cell line amperage has reached more than 100 kA, meeting the growing market demand for refined aluminium product. For processes using combination methods to produce high and ultrahigh purity aluminium, the end-product annual demand typically ranges from hundreds to thousands of tonnes, some order quantity can be much lower, down to the kilogram level. In this niche demand, the larger the cell size, the higher the cost associated with cell shutdown and restart, the longer the recovery period required after component contaminations, and the weaker the rapid adjustment of product variety and output [5]. This need for rapid market responsiveness, combined with objectives of energy saving, environmental protection, and high-efficiency intelligent control, has driven the development of “small-sized and variant” type of three-layer liquid electrolysis processes.

One type is the so-called “compound” integrated cell, or “multi-stage tandem electrolytic cell”. For example, the invention of He Yongdong et al. [34] connects one two-layer liquid electrolytic compartment with multiple three-layer liquid compartments in series. This design reduces the frequency of aluminium melt transfers, thereby minimizing contamination and heat loss by decreasing the exposed aluminium melt surface area, enabling the production of aluminium of varying grades (4N to 6N).

Similarly, the invention by Huimin Lu et al. [35] (see Figure 1) divides the cell chamber into two three-layer molten regions on the left and right by an insulating partition. The bottom is interconnected by aluminium-copper alloy melt. The electrolysis process is effectively equivalent to two series-connected three-layer liquid electrolysis cells: 2N7 primary aluminium undergoes electrolysis at left side of the partition, followed by a secondary electrolysis on the right side, ultimately producing aluminium exceeding 5N. The cell achieves a specific energy consumption of 10 kWh/kg Al, representing a 30 % energy saving compared to conventional three-layer liquid electrolytic cells. Furthermore, no need for casting aluminium cathodes and less anode and cathode replacement and cleaning may reduce labour intensity by 80 %.

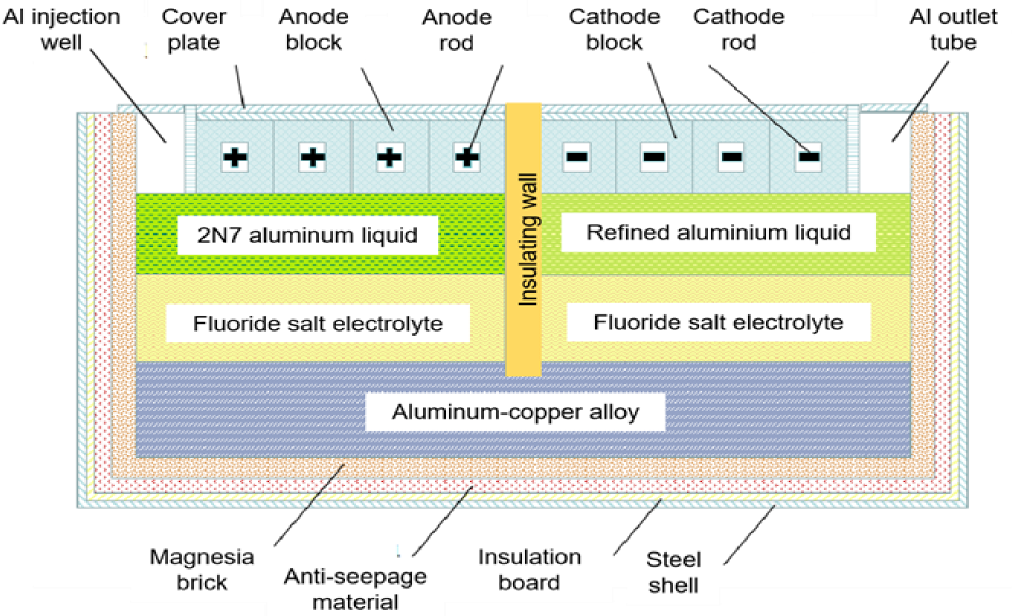

Figure 1. A high purity aluminium electrolysis cell [35].

Another improvement is the so-called “two-layer liquid” electrolysis cell. For example, the invention by Ming Jia et al. [36] (see Figure 2) locates both the Al-Cu alloy and refined aluminium at the bottom of the cell chamber, separated by an insulating wall, and the upper layer of the alloy and the refined aluminium are both covered by a continuous electrolyte melt. The advantages of this design are:

1) The Al-Cu anode alloy may be replaced by 2N6 primary aluminium, reducing raw material costs and simplifying the aluminium addition process;

2) The insulating wall prevents the mixing of anode alloy and cathode aluminium melts; Current is introduced and extracted from the bottom electrode eliminating the electrode replacement operations, allowing the electrolyte to form an intact top crust, thereby significantly reducing heat dissipation and emissions of harmful gases from the cell top;

3) This cell can produce refined aluminium with purity levels ranging from 3N8 to 4N7;

4) The top layer electrolyte melt, on one hand, plays the role of a good seal to drastically reduce the oxidation of the lower aluminium melt and on the other hand substitutes densifiers such as BCl_2 and BF_2 with LiF [37] which can improve melt conductivity and lower the primary crystallization temperature, thereby minimizing electrolyte and cell lining damages caused by hydrolysis products such as hydrochloric acid.

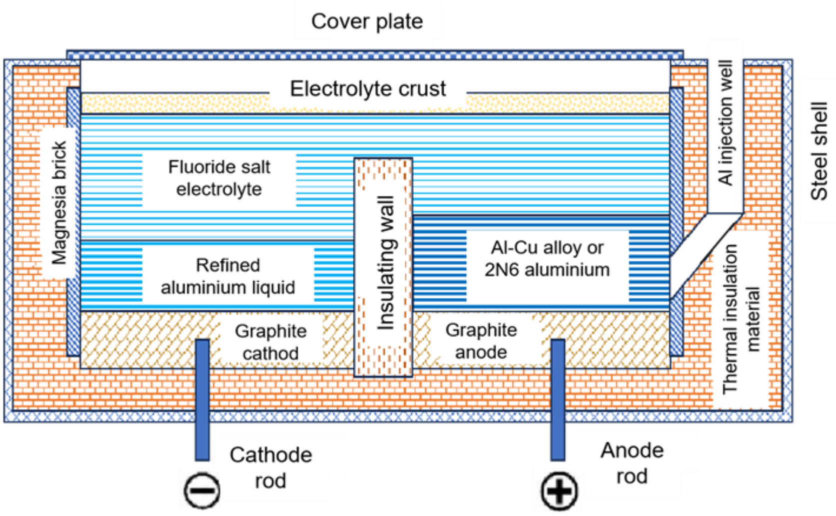

Figure 2. An electrolysis refining cell for high purity aluminium production [36].

To enhance the reaction speed and the production capacity of refined aluminium, DeYoung et al. [38] from Alcoa Inc. invented a new cell type with, apart from traditional horizontal electrode, but also vertical electrode crossed arrangements (see Figure 3). The anode plates extending upward from the bottom anode and the cathode plates extending downward from the top cathode (both in even numbers) overlap in the electrolyte melt and are arranged at certain intervals (polar distance). This structure increases the interpolar area for ion polarization and deposition reactions in the electrolyte melt, significantly improving the output efficiency of refined aluminium, Both the anode and cathode plates are made of materials such as TiB_2, HfB_2, and SrB_2 that have good wettability to aluminium melt, so the aluminium-copper alloy at the bottom of the cell can be adsorbed along the surface of the anode plates to the overlapping area, and the refined aluminium produced on the cathode plate surface can be adsorbed to the top refined aluminium enrichment layer. The product purity can reach up to 99.999 %, and the energy consumption per unit product can be reduced to less than 10 kWh/kg Al. The anode sludge produced can be removed from the cell access channel.

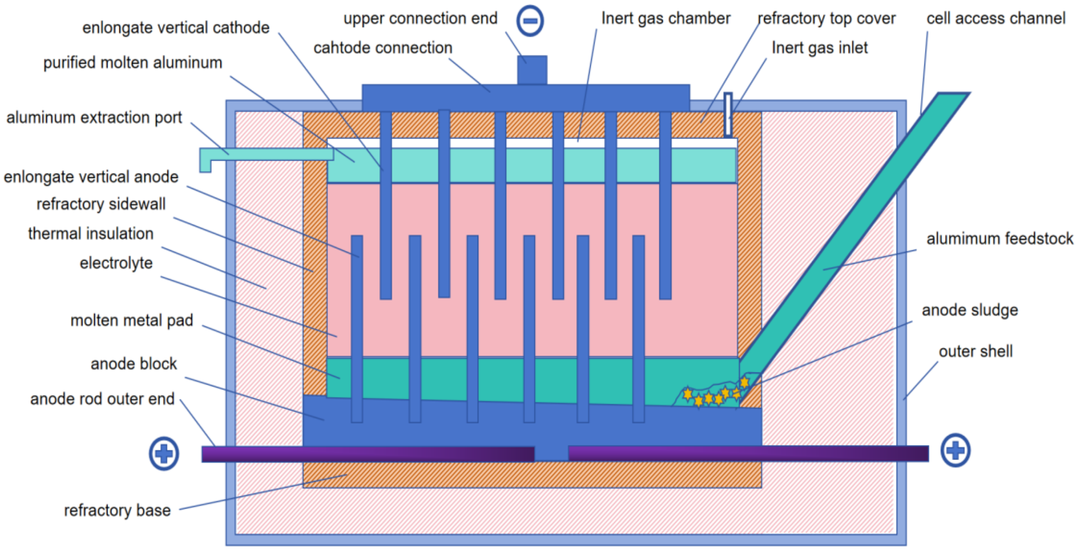

Figure 3. A three-layer liquid electrolysis cell with both horizontal and vertical anode and cathode arrangements [38].

Another invention replaces the traditional vertical layering of molten materials with lateral or annular-centre layering. For example, Zheleznov et al. [39] invented a three-layer liquid electrolysis cell with a detachable, porous, permeable diaphragm (see Figure 4). The electrolyte melt allows unidirectional permeation between the anode aluminium alloy and the cathode refined aluminium, so transforming the conventional vertical layering into an annular-centre layering. Aluminium tapping channels are located at walls of the cathode tube to direct the refined aluminium into the collection tank. This invention enables visualization management and operation of all three molten layers, improving production efficiency as well as the ability to replenish and adjust the electrolyte composition.

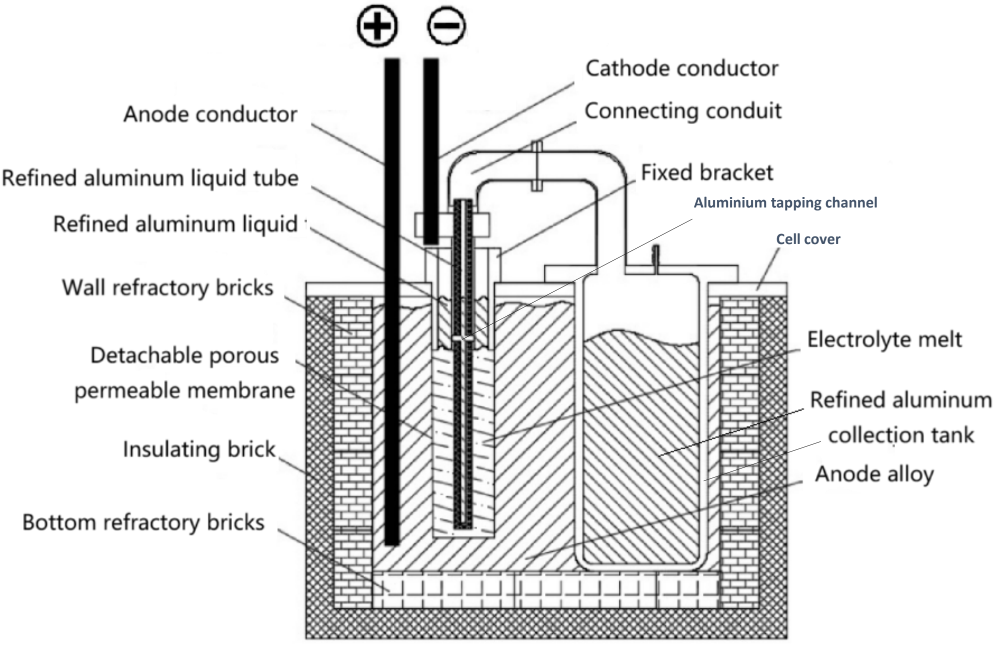

Figure 4. Three-layer liquid electrolysis cell with a unidirectional permeable membrane [39].

5.2 New Applications of Three-Layer Liquid Electrolytic Process: Preparation of High purity Alloys and Recycling of Secondary Aluminium Alloys

Taking advantage of the high purification efficiency of products from three-layer liquid electrolysis, it is possible to realize the co-eutectic preparation of high-value specialty alloys as well as the extraction of valuable elements from secondary alloys. For example, Sheng Yang et al. [40] utilized existing three-layer liquid electrolysis cells by adding scandium chloride or scandium fluoride to the electrolyte to directly electrolyze and produce aluminium-scandium intermediate alloys. Bajmakov et al. [41] employed waste alloys such as Al-Cu-Sn as anode alloys in three-layer liquid electrolysis cell, enabling lossless extraction of aluminium and tin without causing environmental pollution.

5.3 Waste Recycling in Three-Layer Liquid Electrolysis

One of the challenges faced by three-layer liquid electrolysis is the disposal of waste anode alloys and spent electrolyte. Although copper and aluminium in the waste anode alloys are valuable materials, impurity element enrichment (anode sludge) forces them to be sold at low prices.

Feasible recycling routes include removing impurity elements to produce reusable aluminium-copper anode alloys or utilizing the impurity elements to prepare high-value aluminium alloys. The spent electrolyte contains a high concentration of fluorides, chlorides, and other compounds, which increase the cost of hazardous waste treatment. However, how to achieve efficient purification or high-value utilization of the spent electrolyte-turning waste has not yet attracted sufficient attention from researchers.

6. Conclusion

The three-layer liquid electrolysis process for refined aluminium faces an industrial dilemma due to its high energy consumption, high emissions, and limitations in product grade, resulting in ~~it~~ being increasingly displaced by segregation processes. This paper, through a comparative analysis of the advantages and disadvantages of two aluminium refining technologies, proposes approaches such as:

1) Developing high-conductivity, anti-aging, and environmentally friendly electrolyte systems;
2) Achieving high levels of automation and intelligence in the electrolysis process;
3) Developing new corrosion-resistant cell lining materials to extend cell life and seeking advantageous industrial chain combinations.

These strategies aim to significantly reduce energy costs, minimize pollution emissions, and improve product grade and competitiveness. Additionally, the feasibility of upgrading three-layer liquid electrolysis technology is discussed by exploring the development of new “small-scale” variant three-layer liquid electrolysis cells and new applications such as the preparation of high purity alloys from waste anode alloys and spent electrolyte regenerating treatment.

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