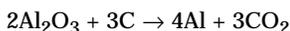


VERONICA and TINOR 2000

New Technologies for Aluminum Production

by Vittorio de Nora

The technology for the production of aluminum by the electrolysis of alumina, dissolved in molten cryolite at temperatures around 950°C, is more than one hundred years old. The process, conceived almost simultaneously by Hall¹ and Héroult, which can be expressed



has not undergone the same process evolution that other large electrochemical processes have, such as the electrochemical production of chlorine and caustic soda from brine.

The Hall-Héroult cell produces aluminum by the electrochemical reduction of alumina (Al₂O₃) dissolved in molten cryolite, which is the only acceptable solvent for Al₂O₃. The process uses consumable carbon anodes fabricated from petroleum coke and pitch, and the carbon cathodes are covered with a pool of molten aluminum. Despite significant technological advancements, the Hall-Héroult process remains basically the same as it was more than one hundred years ago. The main problems in the Hall-Héroult process are related to (1) the high consumption of electrical power (13 to 15 kWh/kg Al); (2) CO₂ emissions due to carbon anode consumption (the actual consumption of the anode is as much as 450 kg/ton of aluminum produced, which is more than 1/3 higher than the theoretical amount of 333 kg/ton); (3) perfluorinated carbon (PFC) compounds produced at the anode; (4) disposal of cyanide contaminated spent potlining; and (5) unpleasant working conditions, mainly in the carbon anode production plant. The energy efficiency of the process can be below 50% due to limitations in cell design imposed by the materials available today. In particular, the instability of the aluminum pool, resulting from intense magnetic fields, imposes a large anode-cathode distance (ACD) and therefore leads to high energy losses. Figure 1 is a schematic view of a Hall-Héroult cell.

A critical environmental and design issue is the replacement of the consumable carbon anode with a non-consumable, dimensionally stable anode. Scientists have tried to replace the carbon anodes but, until now, nobody has succeeded. The most likely non-carbon anode materials that would be resistant to oxygen formation are the oxides. However, all oxides are soluble in cryolite to some degree. Other processes that have been suggested were based on the use of aluminum chloride or silicates as raw materials, but problems related to these processes prevent their utilization.

Aluminum Industry Background

The magnitude of the energy use and environmental problem in the Hall-Héroult process is directly related to the size of the primary aluminum industry. In 2001, 12 companies within the United States produced 2,600,000 metric tons (t) of aluminum and world-wide production was 23,400,000 t with an approximate value of \$4 billion.² Table I shows the global distribution of aluminum production.

The use of noncarbon anodes in aluminum electrowinning cells would drastically improve the aluminum process by reducing pollution and lowering the cost of aluminum production. During electrolysis in conventional Hall-Héroult cells, the carbon anode is oxidized, evolving polluting CO₂, small amounts of CO and dangerous fluorine-containing gases rather than oxygen. The utilization of a noncarbon anode could permit the formation and evolution of oxygen. Kvande and Haupin state that the highest percent reduction in CO and CO₂ emissions resulting from the use of non-carbon anodes would be possible in plants that use hydroelectric power.³

A European Aluminium Association environmental report, *Environmental Profile Report for the European Aluminium Industry*, gives the emissions profile for the entire chain of events in the

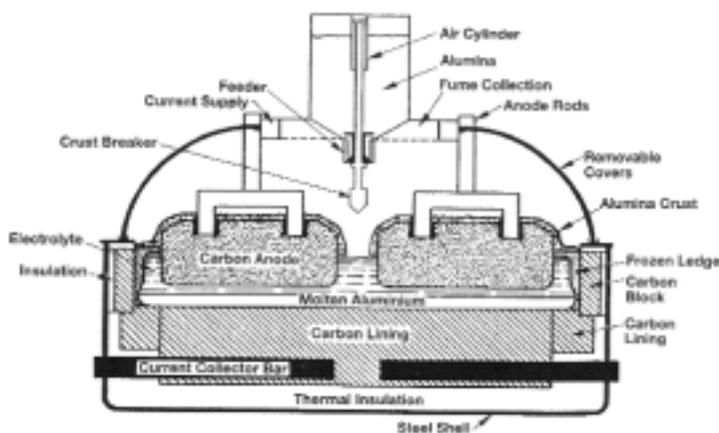


Fig. 1. The Hall-Héroult cell.

Table I. 2001 World Aluminum Production in Metric Tons.

Country	Capacity
Russia	3,200,000
China	2,700,000
United States	2,600,000
Canada	2,500,000
Australia	1,800,000
Brazil	1,200,000
Norway	1,000,000
South Africa	680,000
Venezuela	570,000
France	450,000
Other	6,680,000
Total	23,400,000

Table II. Specific CO₂-Equivalent Emissions from Various Production Processes and Electrical Power Sources for Today's Average Aluminum Electrolysis Cells with Carbon Anodes.

CO ₂ Emissions from Various Production Processes and Electrical Power Sources	Hydro-electric and Nuclear Power Plants	Natural Gas-Fired Power Plants	Coal-Fired Power Plants	Weighted World Averages
CO ₂ from bauxite mining and alumina production	2.0	2.0	2.0	2.0
CO ₂ from pre-baked carbon anode baking	0.2	0.2	0.2	0.2
CO ₂ from electrolysis cells.....	1.5	1.5	1.5	1.5
CO ₂ from equivalent of CF ₄ emissions	2.0	2.0	2.0	2.0
CO ₂ from electrical power production	0	6.0	13.5	4.8
Total Emissions (ton CO₂ /ton Al).....	5.7	11.7	19.2	10.5

Table III. Specific CO₂-Equivalent Emissions from Various Sources for Production of Primary Aluminum in Cells with Inert Anodes.

Emissions from Cells with Inert Anodes	Hydro-electric and Nuclear Power Plants	Natural Gas-Fired Power Plants	Coal-Fired Power Plants	Weighted World Averages
CO ₂ from bauxite mining and alumina production	2.0	2.0	2.0	2.0
CO ₂ from inert anode production	0.2-0.3	0.2-0.3	0.2-0.3	0.2-0.3
CO ₂ from electrolysis cells	0	0	0	0
CO ₂ from equivalent of CF ₄ emissions	0	0	0	0
CO ₂ from electrical power production	0	6.0	13.5	4.8
Total Emissions (ton CO₂ /ton Al).....	2.3	8.3	15.8	7.1

aluminum production process, from producing the energy required for electrolysis, through bauxite and alumina production to carbon anode baking and electrolysis with its process emissions, including those generated by anode effects.⁴ Table II shows CO₂ emissions per ton of aluminum using consumable carbon anodes as a function of electric power source. The weighted world average emission is 10.5 tons of CO₂ per ton of aluminum. Comparable data are given for cells operating with inert anodes, showing a calculated specific emission of 7.1 tons CO₂ per ton of aluminum produced. Table III shows the CO₂ emissions as a function of the electric source. On a world-average basis, an inert anode would represent a 25% to 32% reduc-

tion in overall CO₂ emissions, depending on the energy efficiency of the electrolysis process.³

Research Background

Many patents and technical publications have suggested and described anodes for conventional aluminum electrowinning cells. Sadoway describes anodes for conventional aluminum electrowinning cells provided with an oxide coating containing at least one oxide of zirconium, hafnium, thorium and uranium.⁵ It has also been suggested that to prevent consumption of the anode, the bath should be saturated with the

The MOLTECH VERONICA Metallic Anode

materials that form the active surface. However, these surfaces have poor conductivity or are highly soluble and have not been used. Keller has described a method of producing aluminum in a conventional cell using massive metal oxide anodes having a central vertical through-opening for feeding anode constituents and alumina into the electrolyte, to slow dissolution of the anode.⁶ Duruz, Derivaz, Debely, and Adorian have described metal anodes for aluminum electrowinning coated with a protective coating of cerium oxyfluoride, formed *in situ* in the cell or pre-applied. This coating was maintained during electrolysis by the addition of small amounts of a cerium compound to the molten cryolite electrolyte.⁷ This made it possible to protect the surface from electrolyte attack and, to a certain extent, from gaseous oxygen but not from nascent monoatomic oxygen.

Thonstad and Olsen⁸ suggest that the best choice of inert anode material may be a ceramic, cermet, and metal substrate with an oxide outer layer, but they raise serious questions related to cell design and operation with inert anodes, including metal contamination and engineering problems, especially those related to drained cell configurations. This paper is part of a special section in the May 2001 edition of *Journal of Metals*, which is interesting as background for important topics relating to the use of inert anodes in aluminum electrowinning cells. Also of significance are the contributions of Thonstad and Olsen on nickel ferrite materials,⁹ and the contributions of Theodore R. Beck,¹⁰ and John N. Hyrn and Donald R. Sadoway.¹¹

The goal of much of the above research was to create dimensionally stable noncarbon anodes with the following characteristics: (1) a large surface area, low solubility in the electrolyte, and a high electrochemical activity for the evolution of oxygen, permitting the fast release of oxygen gas and circulation of alumina-rich electrolyte between the anodes and a facing cathode; (2) a design permitting an enhanced electrolyte circulation and which is easy and economic to fabricate into complex shapes; and (3) a long lasting anode material leading to commercially acceptable aluminum production.

Chemical Composition—MOLTECH has devoted extensive time and resources to develop a new advanced aluminum technology to reduce pollution and increase productivity in the production of aluminum. MOLTECH is the only company to have succeeded in making non-carbon metallic anodes with a long-lasting oxide active surface that has a very low solubility in cryolite at slightly reduced operating temperatures in the range of 880° to 930°C.

The VERONICA Anode, operating at a slightly reduced bath temperature, uses the TiB₂-based MOLTECH TINOR 2000-coated drained cathode surface wetted by aluminum. Figure 2 shows a picture of the VERONICA anode. The VERONICA composition is a metal alloy material based on Ni - Fe alloy plus specific additives, such as Cu, Al, Ti, Y, Mn, Si, in order to improve oxidation resistance, suppress grain boundary oxidation/corrosion, control diffusion, improve scale/coating adherence, and obtain the desired electrochemically active surface. The electrochemically active surface is obtained by self-forming an oxide scale after thermal pre-treatment or by an external coating based on iron oxide.

VERONICA Design and Shape—The metallic structure of VERONICA, Fig. 2, is a series of parallel horizontal anode rods, each having an electrochemically active surface on which, during electrolysis, oxygen is anodically evolved. The electrochemically active surfaces are in a generally co-planar arrangement to form the active anode surface. The anode rods are spaced apart to form longitudinal flow-through openings for the fast escape of anodically evolved oxygen, thereby facilitating the flow of alumina-rich electrolyte to an electrolysis zone between the anodes and the cathode and/or the flow of alumina-depleted electrolyte away from the electrolysis zone. A substantially uniform current distribution can be provided from a current feeder through conductive transverse metallic connectors to the anode members and their active surfaces. The use of the anode in a MOLTECH 20-kA pilot drained cell is shown in Fig. 3.



Fig. 2. The MOLTECH VERONICA Metallic Anode.



Fig. 3. The MOLTECH 20-kA pilot drained cell.

The shape of VERONICA is very important because the anode's stability is controlled by the alumina concentration at the anode surface. An optimal design is required to supply alumina-rich bath to the active anode surface, as well as to permit quick gas release of the oxygen bubbles formed at the active surface in order to reduce the overvoltage.

The VERONICA metallic anode is fabricated by cost-effective casting of its metallic alloy material, which also permits simple attachment to the anode stem.

Mathematical modeling of bath circulation around the anode elements and all over the cell was necessary in order to find the optimal design for the anode. Two and three dimensional modeling and analysis of the VERONICA design also included an analysis of the local current distribution, estimations of the global current, and potential distribution for suggested anode designs. It is important that the current density distribution is uniform in order to avoid depletion of oxide ions, which results in dissolution of the active anode surface and eventually corrosive attack of the melt on the substrate. The modeling simulations show that the VERONICA geometry offers a large surface area, which gives a low and uniform current density distribution. The primary current distribution models have been used in three dimensions in order to estimate the global current density distribution and the voltage losses in the VERONICA anodes as used in a full-scale industrial cell.

The simulations also show that the positioning of the rods offers excellent gas release properties. In addition, before the start-up of the 20-kA pilot drained cell, computational fluid dynamics (CFD) studies of bath circulation were also performed, using two commercial codes and models in order to investigate and benchmark drained cell operating characteristics. Bath circulation rate and circulation patterns are important to the maintenance of the high alumina concentrations required on the active surface of the anode, and also to combat bath freezing near the cathode surface. For example, simulation runs were performed with immersion depths of the anode as the variable. The results gave an indication of the optimum bath depth above the anode rods in order to have the desired high bath circulation rates. Figure 4 shows a simulation of bath circulation around the VERONICA rods.

Other Important VERONICA Characteristics—Other VERONICA characteristics important for the commercial utilization of inert anodes include low electrical resistivity and

high thermal stability. Anode lifetime is also very important because it is the key to the purity of the aluminum produced.

MOLTECH results suggest that with an inert anode life of 6 months, already demonstrated in tests completed in 1000 A cells, metal purity is expected to be sufficient, without additional purification, for most commercial applications. Table IV is a list of many of the important material and design characteristics required for the commercial viability of an inert anode.

TINOR 2000—Metallic Anodes are most efficient when used in drained configuration cells having perfectly wetted durable cathode surfaces to provide cathode protection and to permit draining over the lifetime of the cell. MOLTECH TINOR 2000 cathode coating achieves this required level of wettability and makes drained cell configurations possible in both retrofitted Hall-Héroult cells and cells of new design to substantially improve cell performance, increase cell life and decrease aluminum production costs.

When applied to amorphous, semi-graphitized, and graphite cathode blocks, TINOR 2000 has excellent adherence, electrical conductivity and erosion resistance. TINOR 2000 also controls sodium penetration into the cathode.

When using graphitized or semi-graphitized cathode blocks to achieve the substantial benefit of decreased cathode voltage drop, the resulting risk of reduced cathode life can be prevented by coating them with TINOR 2000.

These important advantages of TINOR 2000 mean that cell stability is achieved early; cathode block aging, deformation, and erosion are reduced; there is a more uniform current distribution over the cathode; and the formation of sludge and hard muck is reduced.

VERONICA Cost-Benefit Analysis—One of the advantages of the VERONICA metallic anode is the possibility to recuperate approximately 50% of the value of the materials used, *i.e.*, \$450. With an estimated cost of \$1,200 per 100 kg, which is the weight per anode of VERONICA, the total cost of VERONICA would be approximately \$750. With an operating current density of 0.8 A/cm² and a life of 6 months, the aluminum production per VERONICA anode would be 5.6 t, having a value of approximately \$7,000. Therefore, the cost of VERONICA equals 10.7% of the aluminum production costs (\$1,250 per t aluminum), corresponding to a savings of \$134 in production costs.

The VERONICA metallic anode has demonstrated at the 1000 A scale an underlying wear rate of 3.5 mm/year at the

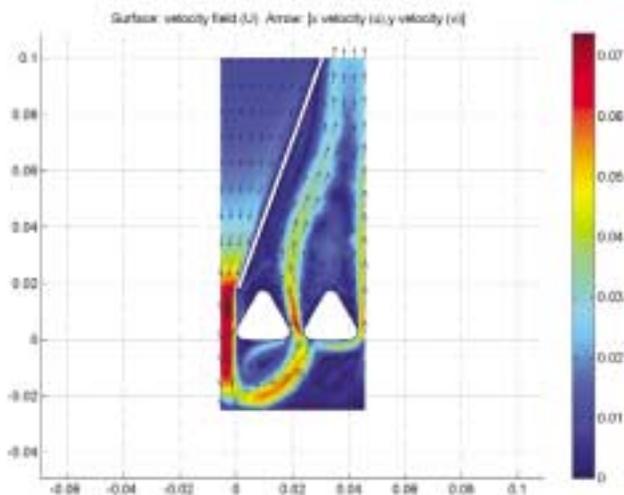


Fig. 4. A simulation of bath circulation around the VERONICA rods.

Table IV. Important Material and Design Characteristics for Inert Anodes.

- Low solubility in molten cryolite-alumina bath
- Resistance to the oxygen produced at the anode
- Resistance to fluoridation
- Thermal stability and mechanical strength
- Low electrical resistivity
- Low overvoltage for oxygen evolution
- Acceptable contamination of the aluminum produced
- Easy and stable electrical connections
- Low cost and reliable fabrication into large shapes

active surface, even when operating at $> 1.1 \text{ A/cm}^2$. Larger scale tests will be needed to confirm these values. However, MOLTECH's estimated cost per anode in combination with such wear rates makes plausible the development of a metallic anode that is competitive with carbon anode technology.

The benefits associated with the utilization of inert anodes include the production of aluminum with no carbon oxide emissions and less overall pollution because of the elimination of carbon anodes. This will enable the aluminum industry to assist governments in meeting commitments concerning the reduction of greenhouse gases, while reducing any taxes imposed on aluminum producers because of CO_2 emissions. Using inert anodes will permit cell operation with a reduced anode-cathode distance (ACD), making more efficient cell designs and operating procedures possible, with less cell disturbance than occurs in cells requiring daily carbon anode changes.

Thus, overall production costs can be reduced by utilizing inert anodes with wetted carbon cathodes and drained cell configurations permitting a reduced ACD. These savings can be as much as 20% of total production costs, depending on cell type and local costs. Table V gives a breakdown of these savings, which reflect typical industry average values, rather than any specific smelter cost data. The Table V savings in production costs do not include those related to the ability to retrofit Hall-Héroult cells instead of needing new potline construction, although such savings would also be realized.

Conclusion

MOLTECH development work suggests that many types of Hall-Héroult cell technology could be easily retrofitted to take advantage of the benefits of the MOLTECH VERONICA metallic anode and TINOR 2000 cathode coating in drained cells, including the elimination of carbon anode pollution and the reduction of aluminum production costs. This would require the cooperation of each smelter in the program to complete detailed engineering for each cell type, adapting the cell control and data acquisition systems and conducting full-scale cell tests to make final adjustments in the smelter's cell technology for use in retrofitted drained configuration with VERONICA metallic anodes. MOLTECH has already begun preliminary engineering for new potlines and smelters cell designs. A full-scale prototype potline would need to be built and operated for several years in order to bring the new technology to a commercial level. ■

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Table V. Savings in Aluminum Production Costs when Using MOLTECH VERONICA Metallic Anodes and TINOR 2002 Wettable Cathode Coating.

Savings Component	Savings as a % of Production Cost
Metallic Anode saving (\$100/t Al)	8.0
Energy saving.....	2.5
Increase in current efficiency	1.5
Labor and disposal saving	1.5
Carbon tax not paid	4.0
Cell life increase.....	2.5
Total Estimated Savings	20.0

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About the Author

Vittorio de Nora, born in Italy, earned a doctor's degree in electrical engineering from the Royal Politecnico of Milan and engaged in research at King's College in London and at the Technische Hochschule in Dresden. His work in the field of electrometallurgy at Lehigh University in the United States led to a PhD in chemical and metallurgical engineering. He later lectured in physical chemistry and electrochemistry at his alma mater, the Royal Politecnico.

Actively involved throughout his life in electrochemical research, he is the author of hundreds of worldwide patents. Among his major contributions was the development of Dimensionally Stable Anodes (DSA) for chlorine manufacture that revolutionized the chlorine industry, conserving electrical energy and eliminating or substantially reducing pollution. Dr. de Nora has recently dedicated himself to the development of a non-carbon anode and new drained cell designs, which could also revolutionize the aluminum industry with the utilization of non-polluting, energy-efficient cells.

Dr. de Nora is one of the founders of International Physicians for the Prevention of Nuclear Warfare, which received the Nobel Peace Prize in 1985. Vittorio de Nora is also a Volta Fellow, a Weston Fellow, and a Case Centennial Scholar. He has been elected an Honorary Member and a Fellow of The Electrochemical Society. His other awards include the honorary degree of Doctor of Science conferred by Lehigh University, by Case Western University, and by the University of Cincinnati.

Dr. de Nora has inspired and encouraged research in electrochemistry and has endowed the annual Society Vittorio de Nora Award for distinguished contributions to the field of industrial electrochemistry.